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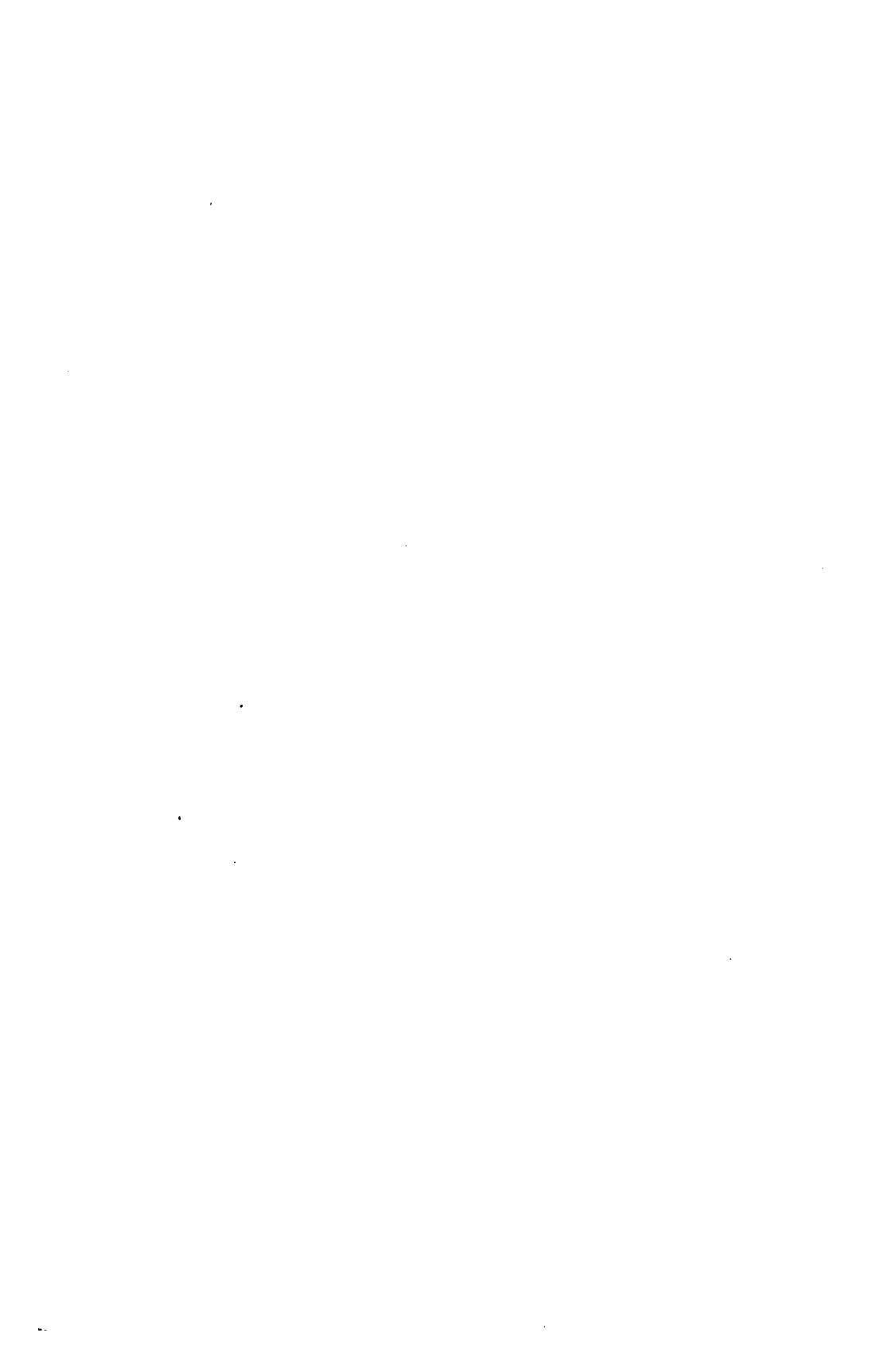


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THE JOURNAL  
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THE ACTION OF IODINE ON SOLUTIONS OF STANNOUS CHLORIDE.

BY S. W. YOUNG AND MAXWELL ADAMS.

Received April 22, 1897.

THE action of free iodine on stannous chloride appears to have been first studied by Henry.<sup>1</sup> He states that when iodine is treated with an excess of a concentrated stannous chloride solution, bright red crystals of stannous iodide separate from the solution on cooling, while on concentration of the mother-liquors straw-yellow needles separate out, which consist of a definite compound, stannous chloro-iodide,  $\text{SnClI}$  or  $\text{SnI}_2\text{Cl}$ . This chloro-iodide was immediately decomposed by water, the crystals turning red, and evidently being converted into stannous iodide, while the stannous chloride went into solution.

If an excess of iodine was used, Henry obtained crystals of stannic iodide, on concentrating the solution. The results of his analyses are not in very good accord with the calculated numbers, which fact he ascribes to the difficulty of the analytical methods. More recently a paper has appeared by V. Thomas<sup>2</sup> concerning the action of dry stannous chloride on a solution of iodine in carbon bisulphide. As the conditions in Thomas' experiments were wholly different from those in ours, his paper need not be further mentioned.

This paper embodies some preliminary results of an attempt to make a more thorough and concise investigation of the reaction. The method of experimentation was as follows: A concentra-

<sup>1</sup> *Phil. Trans.*, 1843, 363.

<sup>2</sup> *Compt. rend.*, 122, 1539.

ted solution of stannous chloride was prepared by the action of concentrated hydrochloric acid on metallic tin. The action was allowed to continue until the evolution of hydrogen became very inconsiderable. This was after about six weeks. During this reaction the solution was protected from the air by a layer of coal oil. It was then rapidly filtered through absorbent cotton and under oil, and kept in this way. The strength of this solution (still containing considerable free hydrochloric acid) was determined as follows:

Ten cc. were diluted to 200 cc. with well boiled water, and twenty cc. portions titrated with standard permanganate solution after the addition of about twenty-five cc. of a one to ten solution of manganese sulphate to guard against the escape of chlorine. The titrations gave closely agreeing results, and the solution was found to contain 0.6818 gram of stannous chloride per cubic centimeter.

Samples for investigation were then prepared by the following method: Ten gram portions of iodine were placed in beakers, and treated with measured volumes of the above solution of stannous chloride, the volumes differing in different samples. The pasty orange-colored mass thus formed was stirred with the addition of small amounts of water from time to time, until the reaction was complete, as indicated by the solution and decolorizing of all the iodine. (No samples containing excess of iodine were prepared.) The action being complete, the beakers and contents were heated on an asbestos plate to boiling, and hot boiled water added until the orange crystalline mass just dissolved. The solutions, on cooling, deposited in most cases needle-shaped crystals, which were rapidly filtered off by suction, dried to some extent quickly with bibulous paper, and finally completely dried *in vacuo* over sulphuric acid. The samples were then carefully powdered and preserved for analysis. All were more or less hygroscopic and some even deliquescent. On long exposure to sunlight the samples experienced some change of color, probably due to oxidation.

#### DESCRIPTION OF SAMPLES.

*Samples OO-A and OO-B.*—In the preparation of all samples, except where otherwise stated, ten grams of iodine were used. In

the preparation of samples OO-A and OO-B, and also of sample O, a solution of stannous chloride containing 0.6902 gram of stannous chloride per cubic centimeter was used. In all others the solution mentioned above and containing 0.6818 gram per cubic centimeter was used. Samples  $OO_A$  and  $OO_B$  were prepared each from ten grams of iodine and 10.6 cc. of stannous chloride, which was just sufficient to decolorize all of the iodine.

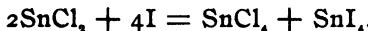
*Sample OO-A.*—Water was added to the sample while hot until the mass of salts dissolved. On cooling, the solution did not deposit any crystals. On standing the solution became dark-colored, owing to iodine being set free from oxidation.

*Sample OO-B* was prepared in exactly the same way, except that the water was not added to dissolve the orange-colored mass, but instead, this was immediately filtered off, washed slightly with water, and analyzed. The analysis gave:

|          | Calculated for<br>$SnI_4$ . | Found. |        |
|----------|-----------------------------|--------|--------|
|          |                             | I.     | II.    |
| I.....   | 81.00                       | 79.45  | 79.43  |
| Cl.....  | ....                        | 1.23   | 1.24   |
| Sn ..... | 19.00                       | 19.68  | 19.64  |
|          | 100.00                      | 100.36 | 100.31 |

On crystallization from glacial acetic acid or carbon bisulfide, the substance gave theoretical numbers for stannic iodide.

In the preparation of these two samples there were present two atoms of iodine for each molecule of stannous chloride. As was to be expected, the reaction is as follows:



*Sample O.*—Ten grams of iodine and twelve cc. stannous chloride. In this preparation there was present a small excess of stannous chloride above that called for in the above equation. Water was added until the product all dissolved on boiling. On cooling the solution deposited a very small quantity of small crystals, which, under the microscope, were seen to be aggregations of needles. Enough for analysis was not obtained. There can be no doubt, however, in the light of the results which follow that these needles were stannous iodide, more or less contaminated with stannous chloride.

*Sample I.*—Ten grams iodine and 14.1 cc. stannous chloride.

On cooling, the solution deposited a considerable quantity of fern-like masses of light orange crystals, which under the microscope were seen to be aggregates of very small needles.

## ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 63.26 | 63.37 |
| Cl ..... | 2.60  | 2.30  |

The percentage of iodine in pure stannous iodide is 68.05.  
This product appears to be somewhat impure stannous iodide.

*Sample II.*—Ten grams iodine and 17.9 cc. stannous chloride.  
On cooling, fine needles similar to sample I were deposited.

## ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 63.48 | 63.46 |
| Cl ..... | 2.47  | 2.52  |

*Sample III.*—Ten grams iodine and twenty-two cc. stannous chloride. Needles similar to I and II, but larger and redder.

## ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 65.13 | 64.99 |
| Cl ..... | 1.65  | 1.98  |

*Sample IV.*—Ten grams iodine and twenty-six cc. stannous chloride. Needles bright red and larger than in III.

## ANALYSIS.

|         |      |       |       |       |
|---------|------|-------|-------|-------|
| I.....  | .... | 65.12 | 64.93 | 65.04 |
| Cl..... | 1.90 | 1.80  | 2.08  | 2.03  |

*Sample V.*—Ten grams iodine and thirty cc. stannous chloride. Crystals like IV.

## ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 65.10 | 64.91 |
| Cl ..... | 2.04  | 2.09  |

*Sample VI.*—Ten grams iodine and thirty-four cc. stannous chloride. Crystals like IV.

## ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 62.08 | 62.00 |
| Cl ..... | 3.60  | 3.63  |

*Sample VII.*—Ten grams iodine and thirty-eight cc. stannous chloride. Crystals like IV.

## ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 63.12 | 63.18 |
| Cl ..... | ....  | 2.59  |

*Sample VIII.*—Ten grams iodine and forty-two cc. stannous chloride. Crystals at first formed appeared to be very similar to those of the preceding preparations. However, after the solution had been allowed to stand for a few hours a curious phenomenon was noticed. A number of very light yellow, almost white, patches appeared in various parts of the mass of red crystals. On close examination these patches were seen to be bunches of radiating needles. These gradually spread until they formed a very considerable portion of the whole. As it was impracticable to separate these crystals from the red ones the following method was used to determine what was the difference between the two sorts of crystals. The preparation was repeated, but in double quantity. After bringing all into solution at the boiling-point, the solution was divided into two approximately equal parts. One (VIII-A) was filtered off as soon as the red crystals had formed, and before the white bunches appeared. The other (VIII-B) was allowed to stand for about twenty-four hours. At this time the white patches had appeared in very considerable quantities. The sample was then filtered off and the crystals thoroughly mixed. Analysis would show whether the red and yellow crystals had the same or different composition.

## SAMPLE VIII-A. ANALYSIS.

|         |       |       |       |       |
|---------|-------|-------|-------|-------|
| I ..... | 59.02 | 59.00 | 59.03 | 59.17 |
| Cl..... | ....  | 5.01  | ....  | 4.96  |

## SAMPLE VIII-B. ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 43.40 | 43.55 |
| Cl ..... | 12.79 | 12.75 |

*Sample IX-A and IX-B.*—Twenty grams iodine and ninety-two cc. stannous chloride, divided into two parts, as in the preceding. In IX-B, before filtering the light yellow crystals had almost wholly replaced the red ones.

## SAMPLE IX-A. ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 61.63 | 61.76 |
| Cl ..... | 3.34  | 3.45  |

## SAMPLE IX-B. ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 42.60 | 42.70 |
| Cl ..... | 14.20 | 14.35 |

*Samples X-A and X-B.*—Twenty grams iodine and 100 cc. stannous chloride divided into two portions.

Products similar to preceding, except that yellow patches appeared before the solutions were wholly cool. Sample X-A was therefore filtered while still somewhat warm. Sample X-B was almost wholly changed over into the light yellow crystals.

SAMPLE X-A. ANALYSIS.

|          |       |       |       |
|----------|-------|-------|-------|
| I .....  | 56.10 | 56.14 | 56.05 |
| Cl ..... | 6.92  | 6.99  | 6.95  |

SAMPLE X-B. ANALYSIS.

|         |       |       |       |       |
|---------|-------|-------|-------|-------|
| I ..... | 40.09 | 39.83 | 39.99 | 39.80 |
| Cl..... | ....  | 16.03 | ....  | 15.81 |

*Samples XI-A and XI-B.*—19.14 grams iodine and 103.4 cc. stannous chloride. Analogous to preceding, but still greater precaution was necessary to prevent XI-A from becoming converted into the yellow substance before it could be filtered. XI-B was practically all yellow before filtering.

SAMPLE XI-A. ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 58.59 | 58.56 |
| Cl ..... | 5.77  | 5.97  |

SAMPLE XI-B. ANALYSIS.

|          |       |       |
|----------|-------|-------|
| I .....  | 39.57 | 39.51 |
| Cl ..... | 15.64 | 15.64 |

Following is a tabulated statement of the above results, together with certain derived calculations. In the first column is placed the number of grams of iodine used in the preparation of the sample. In the second column are the weights of stannous chloride used. These are calculated by means of the standard of the solution. In the third column (headed R) are the ratios of the numbers of atoms of iodine used to the number of molecules of stannous chloride. Thus the number 1.21 after Sample II means that in the preparation of that sample there were used for each molecule of stannous chloride, 1.21 atoms of iodine. The fourth and fifth columns contain the analytical data, averages being used. Columns six and seven contain the percentages of stannous iodide and of stannous chloride calculated from the percentages of iodine and chlorine. These results add up

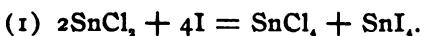
sufficiently close to 100 per cent., when it is considered that errors have been very considerably magnified by the processes of calculation.

TABLE.

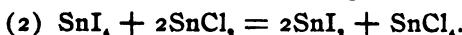
| No. of sample. | I.<br>Grams. | SnCl <sub>2</sub> .<br>Grams. | R.    | Iodine.<br>Per cent. | Chlorine.<br>Per cent. | SnI <sub>4</sub> .<br>Per cent. | SnCl <sub>2</sub> .<br>Per cent. | R'.<br>....* |
|----------------|--------------|-------------------------------|-------|----------------------|------------------------|---------------------------------|----------------------------------|--------------|
| OO-A ....      | 10           | 7.32                          | 2.000 | ....                 | ....                   | ....                            | ....                             | ....         |
| OO-B ....      | 10           | 7.32                          | 2.000 | 79.44                | 1.24                   | ....                            | ....                             | ....         |
| O .....        | 10           | 8.28                          | 1.770 | ....                 | ....                   | ....                            | ....                             | ....         |
| I .....        | 10           | 9.61                          | 1.540 | 63.31                | 2.65                   | 92.60                           | 7.08                             | 14.90        |
| II .....       | 10           | 12.20                         | 1.210 | 63.47                | 2.50                   | 92.83                           | 6.69                             | 14.30        |
| III .....      | 10           | 15.00                         | 0.984 | 65.06                | 1.81                   | 95.15                           | 4.85                             | 10.08        |
| IV .....       | 10           | 17.72                         | 0.832 | 65.03                | 1.95                   | 95.10                           | 5.22                             | 10.87        |
| V .....        | 10           | 20.45                         | 0.723 | 65.00                | 2.06                   | 95.06                           | 5.51                             | 11.50        |
| VI .....       | 10           | 23.18                         | 0.637 | 62.04                | 3.61                   | 90.74                           | 9.67                             | 21.11        |
| VII .....      | 10           | 25.91                         | 0.570 | 63.15                | 2.59                   | 92.34                           | 6.94                             | 14.85        |
| VIII-A ...     | 10           | 28.63                         | 0.515 | 59.05                | 4.98                   | 86.58                           | 13.34                            | 30.59        |
| VIII-B ...     | 10           | 28.63                         | 0.515 | 43.47                | 12.77                  | 63.57                           | 34.20                            | 106.50       |
| IX-A ....      | 10           | 31.37                         | 0.470 | 61.70                | 3.40                   | 90.24                           | 9.11                             | 19.99        |
| IX-B ....      | 10           | 31.37                         | 0.470 | 42.70                | 14.27                  | 62.44                           | 38.20                            | 121.30       |
| X-A ....       | 10           | 34.09                         | 0.433 | 56.10                | 6.95                   | 82.06                           | 18.61                            | 44.93        |
| X-B ....       | 10           | 34.09                         | 0.433 | 39.96                | 15.92                  | 58.45                           | 42.65                            | 144.50       |
| XI-A ....      | 9.57         | 35.25                         | 0.403 | 58.58                | 5.87                   | 85.69                           | 15.71                            | 36.34        |
| XI-B ....      | 9.57         | 35.25                         | 0.403 | 39.18                | 15.64                  | 57.31                           | 41.88                            | 145.00       |

## DISCUSSION OF RESULTS.

It will be noticed that samples I to VII inclusive consist of stannous iodide mixed with small and somewhat variable amounts of stannous chloride. As has been previously stated, the first action of iodine on stannous chloride is to be expressed by the following equation :

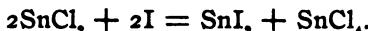


The second step, which occurs when excess of stannous chloride is added, is the reduction of the stannic iodide to stannous iodide by the stannous chloride, according to the equation :



That this reaction is not a complete one appears likely from the fact that even in sample I, where only a very slight excess of stannous chloride over the amount called for in equation (1) is present, this excess is not wholly oxidized, since the crystals which deposit from such a solution contain a very noticeable proportion of stannous chloride (seven per cent.). In sample

III, R is almost exactly unity, and the equation representing the condition at this point is :



That is, if the reaction were complete at this point all of the stannic iodide would have just been reduced to stannous iodide. Since all of the crystals obtained in these preparations contain stannous chloride in significant quantities, it appears, as is suggested above, that the reaction is not complete, but that rather an equilibrium occurs in which stannous and stannic chlorides and stannous and stannic iodides exist side by side. An investigation upon this point is being attempted.

All samples from I to VII, inclusive, show small but significant amounts of stannous chloride (from five to ten per cent.). Samples VIII-A to XI-A (excluding B samples) contain somewhat larger but still variable amounts of stannous chloride. Samples VIII-A and VIII-B differ very markedly from one another, and the same is true of all other A and B pairs. The B samples always contain a much larger amount of stannous chloride than the A samples. It thus appears that the transformation of the red needles into the yellow is accompanied by a very distinct change in composition. Analyses of the yellow needles (B samples) show that they vary considerably in composition (from thirty-four to forty-two per cent. of stannous chloride). Thus the yellow needles are not only different from the red, but they show no constancy of composition among themselves.

Following are the results of some analyses of these yellow bodies (which vary in color from deep yellow to nearly white) which were prepared during some preliminary work on this subject, by using varying excesses of stannous chloride, unfortunately, however, not measured. The excess increased, however, from A to D.

|         | A.    | B.    |       |       |
|---------|-------|-------|-------|-------|
| I.      | II.   | I.    | II.   |       |
| I.....  | 42.27 | 42.25 | 23.26 | 23.33 |
| Cl..... | 13.96 | 14.08 | 29.01 | 28.98 |
| C.      |       | D.    |       |       |
| I.....  | 8.47  | 8.55  | 1.73  | 1.81  |
| Cl..... | ...   | ...   | ...   | ...   |

These results show that by using sufficient excess of stannous

chloride it is possible to obtain crystals that are very low in stannous iodide. It will also be noticed from the results given in the table that the amounts of stannous chloride crystallizing out with the stannous iodide after standing (*i. e.*, in B samples), are roughly proportional to the excesses of stannous chloride used.

These facts led immediately to the conclusion that all these crystalline substances are isomorphic mixtures of stannous chloride and iodide, and that these two salts can form crystals containing the two salts in any proportion. It seems pretty certain that Henry's so-called compound  $\text{SnICl}$  was no true compound, but merely an isomorphic mixture in nearly equivalent proportions, whose occurrence was purely accidental.

The fact that from all the preparations described in the table, the first crystals to form were red, and shown to consist very largely of stannous iodide, while the yellow crystals in those cases in which they formed at all, only came later, and formed slowly and at the expense of the red crystals is due undoubtedly to differences in equilibrium in the solutions at high and at low temperatures. The conditions are such at high temperatures that approximately pure stannous iodide separates. At lower temperatures, providing sufficient stannous chloride is present, the conditions of solubility are such that crystals containing larger amounts of stannous chloride form, while the stannous iodide first formed is slowly redissolved. It appears probable that crystallization from saturated solutions containing both salts presents a somewhat complicated problem in equilibrium, the equilibrium depending upon the relative amounts of the two salts present and upon the temperature as influencing their mutual solubilities.

Aside from facts already discussed there are two others which seem to indicate that such is the case. In the first place, on warming the yellow crystals in their mother-liquor, they turn red. Evidently this is due to the more rapid solution of stannous chloride with increasing temperature. The same result may frequently be attained by treating the yellow crystals with pure water or with a little dilute hydrochloric acid.

In the second place, when a solution of the mixed salts in such proportions that yellow needles will deposit from the beginning (red needles do not form if sufficient excess of stannous

chloride is used) is allowed to deposit by slow cooling, the crystals at the bottom (*i. e.*, those first deposited) are higher in iodine than those on the top. Two such solutions were prepared and allowed to stand. After all crystals had deposited the top portions were dipped out, dried, and analyzed. The same was done with the bottom portions. Following are the results of the analyses :

|        | A.      |       | B.      |       |
|--------|---------|-------|---------|-------|
|        | Top.    | II.   | Top.    | II.   |
| I..... | 40.19   | 40.00 | 40.01   | 40.19 |
|        | Bottom. |       | Bottom. |       |
| I..... | 43.20   | 43.38 | 40.90   | 41.00 |

Investigations are now under way in this laboratory, with the object of throwing some clearer light upon these points.

#### ANALYTICAL METHODS AND NOTES.

1. *Determination of Tin.*—This was determined in only a few cases, it being found preferable to determine iodine and chlorine, than iodine and tin. When tin was determined the method of precipitation as metastannic acid was used, except in a few cases, where but very little chlorine was present. In these cases the weighed sample was treated in a porcelain crucible with two or three cc. of concentrated nitric acid, evaporated to dryness on the water-bath, the residue ignited and weighed as stannic oxide. Total analyses usually fell a little short of 100 per cent. This was undoubtedly due to slight oxidation having taken place in the drying of the samples.

2. *Determination of Iodine and Chlorine.*—Instead of using ferric chloride, as is customary, to set free the iodine, ferric sulphate was used. The iodine was distilled off as usual in the Bunsen apparatus, and titrated with thiosulphate. To the residual liquid (which still contained all the chlorine) ten cc. of a strong solution of potassium permanganate was added, and the distillation was continued into a separate receiver containing potassium iodide solution. The iodine thus set free was titrated with thiosulphate as in the iodine determination. Care is necessary at the beginning of this distillation to prevent some of the solution from being carried over mechanically. The method gives good results, but requires careful manipulation. Hart<sup>1</sup> has already suggested the use of the method qualitatively, and

<sup>1</sup> *Ztschr. anal. Chem.*, 24, 182.

it is likely that White<sup>1</sup> describes the quantitative application of it in much the same form as is given above. The original paper not being at hand this is not positively known.

STANFORD UNIVERSITY, April 15, 1897.

## THE AMOUNT AND PROPERTIES OF THE PROTEIDS OF THE MAIZE KERNEL.<sup>2</sup>

BY THOMAS B. OSBORNE.

Received April 12, 1897.

SOME time since Prof. R. H. Chittenden and the writer published the results of an extended investigation of the proteids of this seed.<sup>3</sup> In that paper no definite statements were made respecting the quantities of the various proteids found, nor were the properties of some of them as fully described as is now possible. For these reasons the results of some additional researches are here put on record.

The proteids of the maize kernel may be distinguished according to their solubilities as follows:

- a. Proteid, soluble in pure water, having some of the properties of proteose.
- b. Globulins, insoluble in pure water, but soluble in salt solutions.
- c. Proteid, insoluble in water and salt solutions, but soluble in alcohol of sixty to ninety-nine per cent.
- d. Proteid matter, insoluble in water, salt solutions and alcohol, but soluble in dilute alkalies and acids.

### a. PROTEID SOLUBLE IN WATER.

If the substance precipitated from an aqueous extract of yellow corn meal by saturating with ammonium sulphate, is dissolved in water and the resulting solution dialyzed, the globulins extracted from the meal by aid of the soluble mineral constituents of the seed are *largely* precipitated. If these globulins are next *completely* removed by heating the solution to 80° and the filtrate therefrom be precipitated by an excess of alcohol, a small quantity of proteid is obtained having many of the reactions characteristic of proteose. A recent determination showed

<sup>1</sup> *Chem. News*, 58, 229.

<sup>2</sup> From the Report of the Connecticut Agricultural Experiment Station for 1896.

<sup>3</sup> *Am. Chem. J.*, 13, 453, 529, and 14, 20. Abstract in Report of Conn. Agr. Expt. Station for 1891, p. 136.

the presence of only 0.06 per cent. of this body. The quantity found was too small for a satisfactory study of the properties of the substance, but the following observations were made. Dissolved in a little water, only a very small quantity of undissolved substance remained, showing the nearly complete removal of proteid coagulable by alcohol. The clear filtrate from this insoluble matter when diluted with an equal volume of distilled *water* gave a considerable coagulum on boiling, but when diluted with the same quantity of *ten per cent. salt solution* only an opalescence resulted on boiling. Nitric acid added to the aqueous solution gave a heavy precipitate which nearly all dissolved on warming, with the production of a strong yellow color, and reappeared on cooling. Saturation of its solution with sodium chloride gave a precipitate much increased by the addition of acetic acid, the filtrate from which was not further precipitated on adding nitric acid. The biuret reaction was violet, not rose red, as is usually given by proteoses. This color reaction, however, was probably modified by the color substance associated with the proteid. Sulphate of copper gave with solutions of this proteose only a turbidity. These reactions do not altogether agree with those given by the proteoses which result from the action of enzymes on native proteids. It is possible that future investigation will show that the so-called proteoses found in seeds belong to a different order of proteids from those usually formed by proteolysis.

In the paper already referred to, a substance is described as albumin which was obtained from solutions that were supposed to have been freed from globulin by prolonged dialysis, by adding thereto ten per cent. of sodium chloride and precipitating with very dilute hydrochloric acid. My recent experience in investigating plant proteids has shown that it is extremely difficult and in many cases impossible to completely precipitate all of the very soluble globulins by dialysis, and since the composition of the so-called albumin thus obtained agreed quite closely with that of a very soluble globulin separated from these solutions by prolonged dialysis, and also since the globulin and the so-called albumin coagulated at about the same temperature, I now feel convinced that the two substances are identical, the latter being a part of the globulin which was not precipitated by

dialysis. In the former paper attention was called to the fact that this body, in some respects, resembled a globulin more closely than an albumin.

In the former paper were also described, as albumin, coagula obtained by concentrating solutions supposed to have been freed from globulin by dialysis and heating to 100°. It was there suggested that these coagula were probably alteration products of the proteids in solution. Since then "proteoses" from many different seeds have been found to yield coagula under similar conditions. It seems therefore quite certain that no true albumin exists in maize kernel.

#### *b. PROTEIDS SOLUBLE IN SALINE SOLUTIONS.*

If an aqueous extract of yellow corn meal is dialyzed for some time, a proteid, having the properties of a globulin, is precipitated which was found to have the following composition:

| <b>MAYSIN.</b> |        |
|----------------|--------|
| Carbon .....   | 52.68  |
| Hydrogen ..... | 7.02   |
| Nitrogen ..... | 16.76  |
| Sulphur.....   | 1.30   |
| Oxygen .....   | 22.24  |
|                | <hr/>  |
|                | 100.00 |

In our paper on the proteids of this seed, Prof. Chittenden and myself designated this globulin "maize myosin." Further study of plant proteids has shown that no sharp distinction can be drawn between plant myosin and plant vitellin, and I now propose to call this proteid *maysin*, in reference to the specific botanical name *mays*. This globulin readily loses its solubility in saline solutions after precipitation, and therefore the amount present in the seed was underestimated in our former paper. A recent determination in yellow corn meal gave 0.25 per cent.

This proteid is readily soluble in very dilute saline solutions so that it is completely extracted from corn meal by water. Dissolved in ten per cent. sodium chloride brine it is coagulated by heating to 70°.

After separating maysin from the extract of corn meal by dialysis, further prolonged dialysis throws down a small quantity of another globulin having the following composition:

## MAIZE GLOBULIN.

|               |        |
|---------------|--------|
| Carbon.....   | 52.38  |
| Hydrogen..... | 6.82   |
| Nitrogen..... | 15.25  |
| Sulphur.....  | 1.26   |
| Oxygen.....   | 24.29  |
|               | <hr/>  |
|               | 100.00 |

This is the globulin which seems to be identical with the "albumin" which was formerly obtained by precipitation with salt and acid. This proteid was found in very small amount, twenty-five kilos of fine meal yielding only four and one-tenth grams by dialysis and three and four-tenths grams by precipitation with salt and acid, that is, seven and five-tenths grams in all or 0.03 per cent. of the meal. This figure cannot be taken as representing quite accurately the total quantity present, for doubtless some was lost in consequence of the globulin becoming insoluble and some also through incomplete extraction. The total quantity, however, is exceedingly small, probably not more than 0.04 per cent.

Dissolved in ten per cent. sodium chloride solution, this globulin coagulates on heating to 62°.

If yellow corn meal, after thorough extraction with water, is treated with ten per cent. salt solution, a further quantity of globulin is extracted, which is readily precipitated by dialysis in well developed spheroids.

This globulin, formerly designated maize vitellin, agrees in composition and reactions and is, doubtless, identical with edestin which I have found in various seeds.

A recent determination of edestin in the seed of yellow corn showed the presence of but 0.06 per cent. The quantities obtained in the former investigations were 0.06, 0.10 and 0.10 per cent. The composition of this globulin is as follows:

## MAIZE EDESTIN.

|                |        |
|----------------|--------|
| Carbon .....   | 51.43  |
| Hydrogen ..... | 6.86   |
| Nitrogen ..... | 18.06  |
| Sulphur .....  | 0.86   |
| Oxygen .....   | 22.79  |
|                | <hr/>  |
|                | 100.00 |

Edestin is much less soluble in saline solutions than the two globulins previously described, and for this reason is readily precipitated by dialysis or dilution. In warm dilute salt solutions it dissolves freely, but on cooling, separates more or less completely, according to the temperature and the strength of the salt solution. Dissolved in ten per cent. sodium chloride brine, it is partly coagulated by heating above 90°, but even on boiling the coagulation is far from complete.

#### c. PROTEID SOLUBLE IN DILUTE ALCOHOL.

Finely ground maize meal when extracted by hot alcohol loses eight-tenths per cent. of nitrogen, equivalent to five per cent. of the characteristic proteid called maize-fibrin by Ritthausen, but first described by Prof. Gorham, of Harvard University, in 1821, and named by him zein. The composition of zein, as shown by the average of nine closely agreeing analyses of as many preparations, is the following :

| ZEIN.          |        |
|----------------|--------|
| Carbon .....   | 55.23  |
| Hydrogen ..... | 7.26   |
| Nitrogen ..... | 16.13  |
| Sulphur.....   | 0.60   |
| Oxygen .....   | 20.78  |
|                | <hr/>  |
|                | 100.00 |

Zein is in many ways a remarkable proteid. It dissolves abundantly in ethyl alcohol of 0.820 specific gravity, forming solutions which, on evaporation in thin layers, leave a perfectly transparent sheet of the proteid.

In *absolute* alcohol, as also in water, zein is wholly insoluble, but in mixtures of water and alcohol it dissolves to a greater or less extent, according to the proportions of the two liquids. It is most soluble in alcohol of from eighty-five to ninety-five per cent., and dissolves but little in alcohol of less than fifty per cent. Solutions of zein in diluted alcohol deposit the proteid on evaporation as the proportion of water in the solution increases. Strong alcoholic solutions of zein gradually coagulate to transparent jellies, which, on long standing, become hard and solid. In ninety-five per cent. methyl alcohol and in commercial propyl alcohol hydrate, zein dissolves readily.

In concentrated glycerol, zein is freely soluble on heating to

about 150° C., to solutions which, when much is dissolved, solidify on cooling to 20°. In such solutions zein can be heated to 200° C. without undergoing any apparent change, for, on pouring them into water, the zein separates as a pulverulent precipitate readily and completely soluble in dilute alcohol.

In crystallized phenol, zein is readily soluble on warming, yielding solutions which leave on evaporation clear films of unchanged zein. In glacial acetic acid, zein dissolves in large proportion and is left, by evaporating the acid on a boiling water-bath, in transparent films of apparently unchanged proteid, which readily dissolve in alcohol.

Strong solutions of zein in glacial acetic acid when poured rapidly into water give large coherent precipitates which retain all the original properties of the proteid; if the solution is dilute the zein is, to a greater or less extent, dissolved by the aqueous acetic acid.

In one-half per cent. sodium carbonate solution and in two-tenths per cent. hydrochloric acid, zein is wholly insoluble even when warmed for twenty-four hours at 40°.

In one-tenth to two per cent. caustic potash solution, zein is very readily dissolved and even by heating to 40° for twenty-four hours in such solutions is not converted into "alkali-albumin," for the precipitate obtained by neutralizing solutions so treated is completely soluble in alcohol.

Alcoholic solutions of zein are not precipitated by tannin, picric acid, trichloracetic acid, lead acetate, silver nitrate, mercuric chloride, ferric chloride, or potassium-mercuric iodide. Clear solutions mixed with silver nitrate dissolved in alcohol leave clear films when evaporated on glass, which gradually turn deep red on exposure to sunlight. When hydrochloric acid in considerable quantity is added to a solution of zein in ethyl alcohol containing much silver nitrate, no precipitate is produced until the mixture has stood for some time, when a turbidity gradually develops which is affected but slowly by light. If the mixture of acid, zein and silver nitrate is boiled it becomes turbid at once.

Zein treated with an alcoholic solution of ferric chloride shows no visible change, but if tested with potassium ferricyanide a deep blue solution is formed, showing that the ferric chloride is reduced at once.

Potassium ferricyanide added to the zein solution is not reduced even after standing some hours.

On digestion with pepsin in hydrochloric acid, zein is converted into proteoses and peptones.<sup>1</sup>

According to J. G. C. T. Kjeldahl (*Bied. Centr.*, 1896, 25, 197, from *Forhandl. Skand. Naturfors.*, 1892, 385-390) zein dissolved in seventy-five per cent. alcohol has a specific rotation of  $(\alpha)_D - 35^\circ$  and in glacial acetic acid  $(\alpha)_D - 28^\circ$ .

#### d. PROTEID MATTER SOLUBLE IN ALKALIES.

This was estimated as follows : One hundred grams of very finely ground maize meal which contained 1.54 grams of nitrogen were successively exhausted with two-tenths per cent. potash water and with alcohol. The dried residue weighed seventy-seven grams and contained 0.1645 gram of nitrogen. Accordingly, 1.3755 grams of nitrogen, including that of all the soluble proteids, had been extracted. This amount multiplied by the factor 6.25 gives the total quantity of soluble proteids, *viz.*, 8.5969 grams. Subtracting therefrom the sum of the several proteids previously determined, *viz.*, zein five grams, globulins 0.39 gram and proteose 0.06 gram, there remains 3.1469 grams of proteid insoluble in salt solutions and alcohol, but soluble in dilute potash water.

The alkaline extract obtained in estimating the quantity of this proteid was filtered perfectly clear, neutralized with acetic acid, the precipitate filtered out, washed thoroughly with water and extracted with hot alcohol to remove zein.

The proteid residue was then redissolved in dilute potash water, filtered clear and again precipitated by neutralization with acetic acid and thoroughly washed with water, with hot alcohol, and finally with ether. After drying at 110° the preparation was analyzed with the following results :

|                |       |        |
|----------------|-------|--------|
| Carbon .....   | ..... | 51.26  |
| Hydrogen ..... | ..... | 6.72   |
| Nitrogen ..... | ..... | 15.82  |
| Sulphur.....   | ..... | 0.90   |
| Oxygen .....   | ..... | 25.30  |
|                |       | _____  |
|                |       | 100.00 |
| Ash .....      | ..... | 2.38   |

<sup>1</sup> Chittenden : *Medical Record*, 45, 487.

The results of this analysis do not indicate that this substance has any relation to the other proteids already described. Owing to its insolubility in neutral fluids no characteristic reactions could be obtained, and accordingly nothing more was learned respecting it.

The foregoing statements show that 100 grams of the yellow corn meal contained approximately:

|   |      |   |
|---|------|---|
| Proteid soluble in<br>two-tenths per cent. potash.... | 3.15 | grams containing 15.82 per cent. N. = 0.4983 gms. |
| Zein .....  | 5.00 | " " 16.13 " " = 0.8065 "                          |
| Very soluble globulin .....                           | 0.04 | " " 15.25 " " = 0.0061 "                          |
| Edestin .....   | 0.10 | " " 18.10 " " = 0.0181 "                          |
| Maysin .....  | 0.25 | " " 16.70 " " = 0.0417 "                          |
| Proteose .....  | 0.06 | " " 17.00 " " = 0.0102 "                          |
|   |      | 1.3809 "  |
| Nitrogen undissolved by dilute potash water .....     |      | 0.1645 "  |
| Total .....   |      | 1.5454 "  |
| Nitrogen in meal by analysis.....                     |      | 1.5400 "  |
| Mean percentage of nitrogen in Maize Proteids .....   |      | 16.057  |

### THE COMMERCIAL PREPARATION OF NITRONAPH- THALENES.

BY WILLIAM H. KRUG AND J. E. BLOMÉN.

Received May 15, 1897.

THE manufacture of nitronaphthalenes has of recent years acquired considerable importance in the arts, and particularly in the explosive industry. In this industry it has been utilized in various ways and for different purposes. The late Nobel was the first to point out that the addition of nitronaphthalene to a nitroglycerol explosive, such as nitrogelatin, rendered this practically non-sensitive to concussion, and this property has been and is still widely applied to render the handling of nitroglycerol explosives more safe.

In the manufacture of nitro substitution powders, nitronaphthalene soon replaced the more expensive nitrobenzol as a basis, and a large number of patents were taken out for its use with oxidizing agents alone or with an admixture of sensitizing agents, such as nitroglycerol, picric acid, etc. A third use was found for nitronaphthalene when it was discovered that it seemingly ren-

dered dynamite "non-freezable." Even a small admixture of nitronaphthalene causes dynamite to remain soft to the touch at low temperatures, and it has therefore been extensively used for the manufacture of non-freezing dynamite. It has been proved that this advantage is only chimerical; the addition of nitronaphthalene in no wise changes the properties which are characteristic of nitroglycerol at low temperatures, but in fact adds a new element of danger, as it makes it impossible for the miner to determine whether the dynamite should be thawed before use.

Still another use of nitronaphthalene was taken advantage of in its property of rendering dynamite "fumeless," but this has not yet been definitely proved. In the manufacture of plastic dynamites it has always been difficult to obtain a nitrocellulose which gelatinizes perfectly in the nitroglycerol. An addition of nitronaphthalene will considerably increase the solvent action of nitroglycerol on nitrocellulose, *i. e.*, even higher nitration degrees than trinitrocellulose may be dissolved when nitronaphthalene is added to the nitroglycerol. The vast importance of this property will be realized by any manufacturer who has a large quantity of the expensive nitrocellulose rejected on account of its insolubility in nitroglycerol.

Almost every manufacturer of explosives has been confronted with the problem of preparing nitronaphthalene in a practical and economical way, but has found that very little of practical value has been published on this important subject.

In speaking of nitronaphthalene, a mixture of the nitronaphthalenes is always meant. When the nitronaphthalene is used in conjunction with nitroglycerol its melting-point is of minor importance, but it is desirable to have as high a degree of nitration as possible, since this will retard the momentum of the explosion to a less degree. When used with other sensitizing agents, such as picric acid, it is obvious that the melting-point must be below the decomposition-point of this agent. When it is desired to use a higher nitronaphthalene in this connection it may be accomplished by adding a small amount of mononitronaphthalene, as the latter acts as a solvent of the higher nitro derivatives, and they together will dissolve picric acid, nitrocellulose and the like.

The investigations, which form the basis of this paper, were

undertaken to determine under what conditions the largest yield of suitable nitronaphthalenes could be obtained. The nitro derivatives of naphthalene are generally obtained either by the action of nitric acid alone or mixtures of nitric and sulphuric acids on naphthalene, or for the highest nitro derivatives by renitration of the lower nitronaphthalenes. It has been suggested at different times to prepare the higher derivatives by the nitration of naphthalene-sulphonic acid similarly to the preparation of nitrophenols from phenolsulphonic acid. To ascertain the practicability of this proposition the following experiments were made :

$\alpha$ -Naphthalene-sulphonic acid was prepared by heating naphthalene to 100° C. for about eight hours with one, two, and three times the amount of sulphuric acid required by theory. A fourth preparation was made, using a large excess of sulphuric acid. This last preparation was the only one which appeared free from naphthalene, the substitution being practically complete. It had no odor, was free from naphthalene crystals and gave a clear solution with water.

A quantity of each of these preparations corresponding to ten grams naphtalin, was weighed into flasks and treated in one series with forty grams 36° B. nitric acid, and in another series with thirty grams of the same acid. This strength acid was chosen because it most nearly represents the waste acid recovered in the regaining works of nitroglycerol plants. The stronger acid, 1.42 sp. gr., is so much more expensive that its use is practically out of the question in the commercial preparation of nitronaphthalenes. The action is furthermore so violent when it is used that there is considerable loss of naphthalene through sublimation, and the gain in yield is not proportionally higher. Dilution below 36° B. offers no advantages, as we will show, and is therefore not necessary.

The nitrations were made on a water-bath and were considered complete some time after the red fumes ceased to come off. The resulting mass was melted under water and washed in this state until acid-free. It was then carefully dried on watch-glasses and weighed. When the nitronaphthalenes are used with nitroglycerol or nitrocellulose, it is very important that it should be neutral, and it may even be slightly alkaline. We have

found that this cannot be done with a weak solution of alkali, as it decomposes the product, giving a deep yellow solution. It may, however, be done with a weak solution of sodium carbonate.

The results were :

SERIES I.—FORTY GRAMS 36° B. NITRIC ACID.

| No.                 | Weight of product. | Color.         | Odor.  | Melting-point. | Remarks.               |
|---------------------|--------------------|----------------|--------|----------------|------------------------|
| I                   | 13.3661            | yellow         | strong | 49.0°          | crystalline mass, soft |
| 1A                  | 12.8342            | "              | "      | 50.0°          | " " "                  |
| <b>Mean 13.1002</b> |                    |                |        |                |                        |
| 2                   | 7.6504             | yellow         | strong | 50.0°          | crystalline mass, soft |
| 2A                  | 7.0289             | "              | "      | 52.0°          | " " "                  |
| <b>Mean 7.3397</b>  |                    |                |        |                |                        |
| 3                   | 1.0022             | greyish-yellow | slight | 152.0°         | fine silky crystals    |
| 3A                  | 0.8288             | yellow         | "      | ....           | " " "                  |
| <b>Mean 0.9155</b>  |                    |                |        |                |                        |
| 4                   | 0.0514             | brown-yellow   | none   | ....           | solid crystalline mass |
| 5                   | 0.4830             | pale yellow    | none   | 150.0°         | fine crystals          |
| 5A                  | 1.3017             | "              | "      | ....           | " " "                  |
| <b>Mean 0.8923</b>  |                    |                |        |                |                        |

SERIES II.—THIRTY GRAMS 36° B. ACID.

| No.                 | Weight of product. | Color.         | Odor.  | Melting-point. | Remarks.                  |
|---------------------|--------------------|----------------|--------|----------------|---------------------------|
| I                   | 10.6374            | orange         | strong | 54.0°          | crystalline mass, soft    |
| 2                   | 9.6721             | yellow         | strong | 57.0°          | crystalline mass, soft    |
| 2A                  | 13.6125            | orange-yellow  | "      | 52.0°          | " " "                     |
| <b>Mean 11.6423</b> |                    |                |        |                |                           |
| 3                   | 0.7623             | greyish-yellow | slight | 163.0°         | bulky fine crystals       |
| 3A                  | 0.4714             | yellow         | "      | ....           | " " "                     |
| <b>Mean 0.6169</b>  |                    |                |        |                |                           |
| 4                   | 0.0227             | brown          | none   | ....           | slightly crystalline mass |
| 5                   | 0.8708             | almost white   | none   | 165.0°         | crystals                  |
| 5A                  | 0.3020             | pale yellow    | "      | ....           | "                         |
| <b>Mean 0.5864</b>  |                    |                |        |                |                           |

No. 1. Pure naphthalene.

No. 2. Naphthalene treated with the theoretical amount of sulphuric acid.

No. 3. Naphthalene treated with twice the theoretical amount of sulphuric acid.

No. 4. Naphthalene treated with three times the theoretical amount of sulphuric acid.

No. 5. Naphthalene treated with excess sulphuric acid.

It will be seen that the two series correspond quite closely

in every respect, and that the yield decreases proportionately with the extent of sulphonation. It is therefore impossible under these conditions to prepare nitronaphthalenes from  $\alpha$ -naphthalene-sulphonic acid although a higher nitration degree is obtained than with pure naphthalene. The products obtained with the latter seem to be practically mononitronaphthalene, and previous sulphonation in the other tests was so incomplete that the advantage to be gained by it is not apparent.

We next turned our attention to the preparation of the nitronaphthalenes from naphthalene direct with a view of determining the mixture of nitric and sulphuric acids which would give the best results. Ten grams of naphthalene were used in each experiment. The sulphuric acid was mixed with the nitric acid before adding it to the naphthalene and the amount used corresponded to that present in the tests of the first series.

**SET 1.—30.23 GRAMS NITRIC ACID USED CORRESPONDING TO FORTY GRAMS 36° B. ACID.**

| No. | Weight<br>$H_2SO_4$ . | Weight of<br>product. | Color.       | Odor.  | Melting-<br>point. | Remarks.                  |
|-----|-----------------------|-----------------------|--------------|--------|--------------------|---------------------------|
| 1   | 8.0                   | 14.3470               | orange       | strong | 86.0°              | crystalline mass, soft    |
| 1A  | 8.0                   | 14.2646               | "            | "      | 99.0°              | " " "                     |
|     |                       | Mean 14.3058          |              |        |                    |                           |
| 2   | 16.0                  | 14.5964               | orange       | strong | 116.0°             | crystalline mass, hard    |
| 2A  | 16.0                  | 14.6278               | "            | "      | 124.0°             | " " "                     |
|     |                       | Mean 14.6121          |              |        |                    |                           |
| 3   | 24.0                  | 15.2593               | yellow       | none   | 136.0°             | no visible crystals, hard |
| 3A  | 24.0                  | 14.8473               | "            | "      | 139.0°             | " " "                     |
|     |                       | Mean 15.0533          |              |        |                    |                           |
| 4   | 52.4                  | 16.9195               | light yellow | none   | 112.5°             | no visible crystals, hard |
| 4A  | 52.4                  | 17.2489               | "            | "      | 109.0°             | " " "                     |
|     |                       | Mean 17.0847          |              |        |                    |                           |

**SET 2.—22.67 GRAMS NITRIC ACID USED CORRESPONDING TO THIRTY GRAMS 36° B. ACID.**

| No. | Weight<br>$H_2SO_4$ . | Weight of<br>product. | Color.       | Odor.  | Melting-<br>point. | Remarks.               |
|-----|-----------------------|-----------------------|--------------|--------|--------------------|------------------------|
| 1   | 8.0                   | 14.2030               | orange       | strong | 72.0°              | semi-crystalline, soft |
| 1A  | 8.0                   | 14.3260               | "            | "      | 80.0°              | " "                    |
|     |                       | Mean 14.2645          |              |        |                    |                        |
| 2   | 16.0                  | 13.7764               | orange-brown | strong | 100.0°             | semi-crystalline, soft |
| 2A  | 16.0                  | 13.4370               | deep orange  | "      | 108.0°             | " "                    |
|     |                       | Mean 13.6067          |              |        |                    |                        |

| No. | Weight H <sub>2</sub> SO <sub>4</sub> . | Weight of product. | Color.       | Odor.  | Melting-point. | Remarks.                  |
|-----|---|--------------------|--------------|--------|----------------|---------------------------|
| 3   | 24.0                                    | 15.0656            | yellow       | slight | 129.5°         | slightly crystal'e, hard  |
| 3A  | 24.0                                    | 15.7075            | "            | none   | 136.0°         | " " "                     |
|     |   | Mean 15.3866       |              |        |                |                           |
| 4   | 52.4                                    | 17.7699            | light yellow | none   | 108.0°         | no visible crystals, hard |
| 4A  | 52.4                                    | 16.9200            | "            | "      | 110.0°         | " " "                     |
|     |   | Mean 17.3449       |              |        |                |                           |

SET 3.—27.87 GRAMS OF NITRIC ACID USED CORRESPONDING TO FORTY GRAMS 34° B. ACID.

| No. | Weight H <sub>2</sub> SO <sub>4</sub> . | Weight of product. | Color.        | Odor.  | Melting-point. | Remarks.               |
|-----|---|--------------------|---------------|--------|----------------|------------------------|
| I   | 8.0                                     | 13.4895            | orange        | strong | 84.0°          | crystalline mass, soft |
| IA  | 8.0                                     | 14.2570            | "             | "      | 80.0°          | " " "                  |
|     |   | Mean 13.8733       |               |        |                |                        |
| 2   | 16.0                                    | 14.7964            | deep orange   | slight | 97.0°          | crystalline mass, soft |
| 2A  | 16.0                                    | 15.0230            | "             | "      | 94.0°          | " " "                  |
|     |   | Mean 14.9097       |               |        |                |                        |
| 3   | 24.0                                    | 16.2178            | orange-yellow | none   | 133.0°         | slight'y cryst'l, hard |
| 4   | 52.4                                    | 16.3830            | brown-yellow  | none   | 126.0°         | slight'y cryst'l, hard |
| 4A  | 52.4                                    | 16.7150            | light brown   | "      | 126.0°         | " " "                  |
|     |   | Mean 16.5490       |               |        |                |                        |

SET 4.—20.90 GRAMS OF NITRIC ACID USED CORRESPONDING TO THIRTY GRAMS 34° B. ACID.

| No. | Weight H <sub>2</sub> SO <sub>4</sub> . | Weight of product. | Color.       | Odor.  | Melting-point. | Remarks.                               |
|-----|---|--------------------|--------------|--------|----------------|--|
| I   | 8.0                                     | 13.6220            | orange       | strong | 99.0°          | crystalline mass, soft                 |
| IA  | 8.0                                     | 13.6460            | "            | "      | 85.0°          | " " "                                  |
|     |   | Mean 13.6340       |              |        |                |  |
| 2   | 16.0                                    | 13.7861            | yellow       | none   | 122.0°         | slightly crystalline,<br>somewhat soft |
| 2A  | 16.0                                    | 14.2410            | "            | "      | ....           | slightly crystalline,<br>hard.         |
|     |   | Mean 14.0136       |              |        |                |  |
| 3   | 24.0                                    | 14.4400            | choc'l-brown | none   | 106.0°         | no visible crystals, hard              |
| 3A  | 24.0                                    | 14.9230            | "            | "      | 108.0°         | " " "                                  |
|     |   | Mean 14.6815       |              |        |                |  |
| 4   | 52.4                                    | charred            | ....         | ....   | ....           | tarry, semi-liquid                     |
| 4A  | 52.5                                    | charred            | ....         | ....   | ....           | " "                                    |

The highest yield was therefore obtained in every set except No. 4, when an excess of sulphuric acid was used. In No. 4 so little nitric acid was present that the product was decomposed by the sulphuric acid. The degree of nitration, as characterized by

the melting-point, also increases with the amount of sulphuric acid present, but an excess has the opposite effect. The amount of nitric acid used in Set 1 has no advantage over the smaller amount used in Set 2, but it is not advisable to use still less acid, especially when higher nitration degrees are desired, since the product is apt to be attacked by the sulphuric acid.

To obtain nitro derivatives of naphthalene for commercial purposes, it is therefore best to nitrate the naphthalene with a mixture of nitric and sulphuric acids, using about three times as much 36° B. acid as naphthalene. The amount of sulphuric acid to be used will vary with the nitration degree desired and ranges from 4 : 1 (nitric : sulphuric) for low melting products, to 3 : 2 for the higher derivatives. Too large an excess must be avoided, as it chars the product, producing a tarry useless end-product.

WASHINGTON, D. C., MAY 13, 1897.

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#### SPONTANEOUS COMBUSTION OF MOLASSES.

BY J. T. CRAWLEY.

Received April 5, 1897.

EARLY in September of last year a sample of charred molasses was forwarded to the laboratory of the Hawaiian Experiment Station from the Hamakua Mill, Hawaii, but owing to stress of work it was not examined until quite recently. The following extracts are taken from the letter from Mr. William McQuaid, chemist at the Hamakua Mill, which accompanied the sample. "The molasses in question was boiled to what is known as "string proof," at a temperature of 160°-165° F., and run into an underground cistern from time to time until the molasses was within six or eight inches of the top of the cistern, when the walls cracked, and the molasses began to leak out. The molasses continued to leak for about one and a half months, during which time five or six feet of the molasses was thus lost. That which remained seemed to be in a perfect condition. Five days later, however, it was found flowing over the sides of the cistern in somewhat of a burnt state. The temperature at the point where the molasses flowed over was 92° C., but in the cistern, and especially where the crack was located, this boiling seemed to be more violent.

"This flowing continued for about twelve hours, but the molasses continued boiling within the cistern until there was left

nothing but a few feet of charred mass. The fumes given off affected the eyes very much, and coming in contact with the metal roof formed a salt."

The sample of char formed under the above conditions was tested with a view of establishing the probable degree of heat at which the changes took place, as also to find the origin of the heat. Parts of the sample were quite black, having somewhat a ropy feel and consistency; other parts were dry, brittle, vesicular masses, brownish in color, resembling very much vesicular lava, while still other portions were of a much lighter color, the decomposition having gone so far as to drive off almost all volatile products, leaving a residue of carbon, ash, etc.

Several hundred grams of the material were repeatedly macerated and digested with cold and hot water. A large portion dissolved, giving a very dark colored solution, resembling the solution of caramels. This dark colored substance was still dissolved in notable quantities even after five days' digestion. The water solution was quite acid; therefore a weighed quantity was taken, digested with water, and the filtrate distilled with phosphoric acid. The acid of the distillate proved to be acetic acid almost entirely, with a small quantity of formic acid. The total acid amounted to three and eight-tenths per cent. calculated as acetic acid.

*Sucrose.*—500 grams were extracted with water, sufficient alcohol added to bring the strength of the alcoholic solution to sixty per cent., and precipitated with strontium oxide. The very copious precipitate was filtered, washed, suspended in water, and saturated with carbon dioxide. The filtrate from this precipitate was clarified with lead acetate, the lead thrown out with hydrogen sulphide, and the clear filtrate evaporated. Not a trace of sucrose could be detected either by crystallization or by reduction of copper solution after hydrolysis. This negative result was to be expected, since the large content of free acid taken in connection with the high heat during combustion in the tank, would have broken up the sucrose very quickly.

The distillate, obtained by distilling a portion of the original matter with phenyl hydrazine, gave the characteristic furfural hydrazone, thereby proving the presence of furfural in the original material, but in minute quantities.

On evaporating the water solution of the char, and adding alcohol, a very dense precipitate was obtained, which on purification and hydrolyzing with hydrochloric acid, reduced Fehling's solution, showing the presence of glucose-yielding bodies, or mucilages in comparatively small quantities.

The original sample, on being distilled with hydrochloric acid, gave with phenyl hydrazine the test for furfural-yielding bodies, the gums, in extremely small quantities, thus showing that these bodies, the mucilages and gums, have been almost totally destroyed. In the so-called gums found in the sugar-cane Dr. Maxwell found 64.6 per cent. to be glucose-yielding bodies, or hexosans, and 3.6 per cent. furfural-yielding bodies, or pentosans.

The water-soluble bodies present in the original char were separated by alcohol of different strength into bodies having melting-points varying from 130° C. to 275° C., while others decompose without melting.

The following bodies were detected, the per cent. being given where that was estimated :

|                                |                |                            |
|--------------------------------|----------------|----------------------------|
| Organic acid distilled         | 3.80 per cent. | calculated as acetic acid. |
| Furfural .....                 | .....          | minute quantities          |
| Furfural-yielding bodies ..... | .....          | " " "                      |
| Glucose-yielding bodies .....  | .....          | small " "                  |
| Caramels .....                 | .....          | large "                    |
|                                |                | Per cent.                  |
| Reducing sugars .....          | .....          | 11.20                      |
| Nitrogen .....                 | .....          | 0.87                       |
| Phosphoric acid .....          | .....          | 0.30                       |
| Potash .....                   | .....          | 2.27                       |
| Insoluble in water .....       | .....          | 38.20                      |
| Moisture .....                 | .....          | 15.00                      |

The moisture fumes given off from the burning mass came in contact with a metal roof and formed a salt, a sample of which also was forwarded to this office. The salt was almost pure zinc acetate with a little formate. The formic acid was separated from acetic by digesting their lead salts with alcohol, breaking up the insoluble lead formate with hydrogen sulphide and proving the presence of formic acid by its reducing action on silver and mercury salts.

Taking the original molasses from which this char resulted as having the probable composition,

|              | Per cent. |
|--------------|-----------|
| Water .....  | 20        |
| Sucrose..... | 45        |
| Glucose..... | 10        |

we see (1) that fully eighty per cent. of the sugars present have been destroyed, with a large part of the gums and mucilages; (2) that they have yielded, among other bodies, formic and acetic acid, the latter in large quantities, furfural and caramels of varying degrees of solubility and melting-points; and (3) that a residue of insoluble caramels and unburnt carbon largely, to the amount of fully one-third the weight of the char is left behind.

As to the degree of heat at which these changes took place, we must conclude that at least a temperature of 200° C. was maintained for some time during which the caramel was formed, while a very much higher degree was reached toward the end of the action.

The phenomenon can have been nothing else than spontaneous combustion, the acid products being oxidation products, and therefore having lower thermal values than the original sugars. The successive stages of oxidation and decomposition furnished the heat necessary to carry the whole mass to the next stage.

As to the initial cause of the rise in temperature, little can be said; the high water content and known fluidity of molasses would tend to retard decomposition by oxidation. It is a fact well known among practical sugar-house men, that if a molasses of low grade be boiled at a high temperature and run into coolers it is very apt to froth and foam, and run over the sides of the containers. It is also known that running successive charges of hot molasses into the same container will often result in a burning of the product and foaming over the sides of the container.

The cause of this foaming and frothing is not positively known. Fermentation often proceeds in a very thick molasses, in fact at a much higher density than is generally known, and the escaping carbon dioxide would tend to cause the mass to rise up. I am inclined to believe, however, that in the majority of

cases this frothing is due to decomposition of the non-sugars. This is a subject that will be looked into.

Whatever may have been the initial cause of heat, whether fermentation or decomposition due to the treatment, there can be no doubt that there was a violent manifestation of heat most destructive in its effects.

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### THE FERROCYANIDES OF ZINC AND MANGANESE.<sup>1</sup>

By G. C. STONE AND D. A. VAN INGEN.

Received May 15, 1897.

OUR work on ferrocyanides was undertaken more to try to reconcile the very discordant statements that have been made about its value as a means for the volumetric determination of zinc than to determine the exact composition of the salts. We therefore have merely tried to determine the influence of temperature and acidity on the composition of the precipitates formed when potassium ferrocyanide is added to the solution of a salt of zinc or manganese. The simplest method for this is to add to a known amount of a zinc solution an excess of a ferrocyanide solution, the strength of which has been accurately determined by titration with permanganate and to determine the excess of ferrocyanide not precipitated by the zinc by titration with permanganate. We found that it was practically impossible to filter the ferrocyanides of either zinc or manganese, but by diluting to a known volume, allowing the precipitate to settle and titrating an aliquot portion, we obtained results that agreed with each other, provided the excess of ferrocyanide remained the same; but with varying excesses the ratio of zinc to ferrocyanogen in the precipitate fell irregularly as the excess of ferrocyanide increased. With manganese this method also failed, as we found that the ferrocyanides of manganese were somewhat soluble in water, rather more so in potassium ferrocyanide and entirely soluble in strongly acid solutions.

We next tried precipitating zinc and manganese in neutral, strongly acid solutions, both hot and cold, and in cold slightly acid ones. The precipitates were washed by decantation. Most of them settled very slowly, especially when nearly washed. We found that they settled much more rapidly if some other salt

<sup>1</sup> Read at the meeting of the New York Section, May 7, 1897.

was present, and in most cases added barium chloride, as it caused the precipitate to settle comparatively rapidly and did not react with it. Even then the washing was very tedious, requiring several days. The zinc salts were much easier to wash than the manganese, and it was possible to test the completeness of the washing, as they are not appreciably soluble in water; but with manganese it was impossible to tell when the washing was complete, owing to the solubility of the manganese ferrocyanides. We therefore washed all the manganese precipitates several times more than we found necessary for the zinc, but even then felt somewhat doubtful of the result in some cases.

We found the best test for soluble ferrocyanides was a very dilute solution of cobalt nitrate, so dilute that two or three drops of it on a white porcelain plate showed no color. In applying the test the best way is to put a drop of a dilute solution of cobalt on a watch-glass and shake it off so that only a very minute drop, or no visible *drop* remains, then add two or three drops of water and a few drops of the solution to be tested. Hold the watch-glass at about the level of the eye and look across the surface towards a window; a faint green can be seen if even a trace of ferrocyanide is present. If the cobalt solution is not very dilute, its color, red, neutralizes the green, and it does not show. Testing the delicacy of this reaction with known amounts of ferrocyanide, we found that one cc. of a solution containing 0.000009 gram of potassium ferrocyanide showed a color, when compared with distilled water; but with one containing 0.000007 gram no color could be seen. Ferric chloride is nearly, but not quite, as delicate as cobalt; uranium is much less delicate.

Having washed our precipitates, we dried them and heated a weighed portion in a porcelain crucible, at first gently, then very strongly, to decompose the organic matter; dissolved in hydrochloric acid and boiled with potassium chlorate to oxidize the iron; precipitated the iron by barium carbonate; dissolved the precipitate; reduced the iron by hydrogen and determined it by titration with potassium permanganate. In the filtrate from the iron we determined the manganese by titration with permanganate. The zinc we separated from the excess of barium by pre-

cipitation as sulphide, converted to phosphate and weighed as pyrophosphate; or, we removed the barium as sulphate and determined the zinc as pyrophosphate in the filtrate. The atomic weights used were those given in this Journal, 18, 213 (March, 1896), where oxygen equals 16. They are: Carbon, 12.01; hydrogen, 1.008; iron, 56.02; manganese, 54.99; nitrogen, 14.04; phosphorus, 31.02; potassium, 39.11; and zinc, 65.41. We did not attempt to determine more than the ratio of zinc or manganese to iron, which, of course, is the same as the ratio of ferrocyanide.

A zinc salt precipitated from a neutral solution in the cold, the amount of ferrocyanide used being slightly in excess of what was required to form zinc ferrocyanide with the zinc present, gave a ratio of 287 atoms of zinc to 285 atoms of iron. A second similar precipitate gave a ratio of 702 : 692. In both cases the ratio is practically 1 : 1, giving the empirical formula  $ZnK_2Fe(CN)_6$ .

Two lots precipitated from cold neutral solutions, in which the zinc was in excess, gave ratios of 501 : 511, and 700 : 684, which also gives the formula  $ZnK_2Fe(CN)_6$ .

The next precipitate was formed in a cold solution containing five cc. per hundred of hydrochloric acid. Two portions of this were analyzed giving ratios of 160 : 113 and 318 : 227, or in both cases 100 : 71, this would make the formula  $Zn_{10}K_6(Fe(CN))_6$ , about an average of two of the other salts found.

The next two were precipitated from hot solutions, *A* was neutral and *B* contained five cc. of hydrochloric acid per hundred. *A* gave a ratio of 189 : 136, and *B* of 176 : 135; in both cases nearly 4 : 3, making the formula  $Zn_4K_3(Fe(CN))_6$ .

We precipitated the next lot in a dilute solution containing one cc. of dilute (1 : 6) hydrochloric acid in each hundred, these being the conditions under which we precipitate zinc and manganese in the volumetric method we use. This gave us ratios of 175 : 131 and 174 : 130, giving the formula  $Zn_4K_3(Fe(CN))_6$ .

The last zinc salt which we analyzed was bought from a dealer in chemicals as  $Zn_2Fe(CN)_6$ . It gave us ratios of 169 : 115 and 170 : 116, giving the formula  $Zn_2K_2(Fe(CN))_6$ .

With manganese the results were not quite as satisfactory, owing to the impossibility of being sure that the precipitates

were completely washed. In the precipitates that received the most washing we found the simplest ratios of manganese to iron.

Two lots precipitated from cold neutral solutions, *A* containing more and *B* less ferrocyanide than would form  $Mn_2Fe(CN)_6$ , gave ratios of, *A* 555 : 594, and *B* 941 : 991, slightly more than 1 : 1, making the formula  $Mn_{10}K_4(Fe(CN)_6)_{11}$ , or more probably  $MnK_2Fe(CN)_6$ .

The next were precipitated from cold solutions containing five cc. of hydrochloric acid per hundred; they gave ratios of 155 : 116 and 309 : 233, or 4 : 3, making the formula  $Mn_4K_4(Fe(CN)_6)_{11}$ .

The next solutions were hot, *A* containing five cc. hydrochloric acid per hundred and *B* being neutral. The ratios were: *A* 148 : 161, and *B* 144 : 135, giving the formula  $Mn_{10}K_4(Fe(CN)_6)_{11}$ , and  $Mn_{10}K_4(Fe(CN)_6)_{10}$ ; in both cases it should probably be  $MnK_2Fe(CN)_6$ .

The last of the manganese salts were prepared under the conditions we have in our volumetric method, a cold solution containing one cc. of dilute (1 : 6) hydrochloric acid in one hundred cc. They gave ratios of 141 : 140 and 142 : 140— $MnK_2Fe(CN)_6$ .

It being evident from the preceding that both zinc and manganese form different salts under varying conditions, we next tried whether the different indicators which have been proposed for volumetric analysis showed the same salt, and whether any one indicator showed different salts under different conditions. The indicators which we have seen proposed are ferric salts, uranium, cobalt, copper, and platinum. In testing we used zinc and manganese solutions, in which the metals had been very carefully determined gravimetrically, and a solution of potassium ferrocyanide which had been titrated with permanganate, and the ferrocyanide value calculated from the iron value. The variables were the proportions of acid, the temperature, the dilution of the indicator, and the way the solution and indicator were brought together.

In a cold solution containing one-seventh cc. of hydrochloric acid in one hundred, uranium, when a drop of it was mixed with a drop of the solution on a porcelain plate, showed the reaction when the quantities of zinc and ferrocyanide were sufficient to form  $Zn_2Fe(CN)_6$ .

In a hot solution containing ten cc. of hydrochloric acid,

uranium, used as in the last case, gave the reaction with  $Zn_2K_4(Fe(CN)_6)_2$ .

In a cold solution containing one-seventh cc. of acid, uranium gave a reaction for  $Zn_2K_4(Fe(CN)_6)_2$ , when drops of it and the solution were placed side by side on filter paper so that the uranium did not touch the precipitate, but only the clear solution that filtered from it. Under the same conditions copper and ferric chloride gave the reaction at the same point.

Cobalt was tried, using a strong solution, placing a drop on porcelain and a drop of the solution by it, so that the two touch, but do not mix. The reaction was for  $Zn_2K_4(Fe(CN)_6)_2$ . When the solution was *mixed* with very dilute cobalt, the reaction was for  $Zn_2K_4(Fe(CN)_6)_2$ . Both of the solutions tested with cobalt were cold and contained one-seventh cc. hydrochloric acid per hundred.

Platinum was not tried. Dr. Miller<sup>1</sup> states that when used with a hot acid solution it gives the reaction with  $Zn_2K_4(Fe(CN)_6)_2$ . He says it does not work with a cold solution.

With manganese we tried only three indicators. In all cases the solutions were cold and contained one-seventh cc. of hydrochloric acid per hundred. Strong cobalt and uranium on paper gave the reaction for  $MnK_2Fe(CN)_6$ ; very dilute cobalt gave it for  $Mn_2K_4(Fe(CN)_6)_2$ .

Of the different indicators tried we found cobalt the most satisfactory, as it shows the reaction as soon as the drops touch, while all the others require an appreciable time for it to develop.

It will be seen that all the salts shown by the indicators, all but the third of the zinc series, and, we may add, twenty-three out of twenty-eight, in which we tried to determine the ratios by adding an excess of ferrocyanide and titrating it, are salts having nearly the general formula  $K_nFe(CN)_6 \cdot nR''Fe(CN)_6$ , which is possibly the formula of these salts. Nearly all of those which contain more than one atom of the heavy metal agree fairly with the formula  $R_nK_{2n-4}(Fe(CN)_6)_{n-1}$ , the salt with one atom being the common difference of the series  $R''K_2Fe(CN)_6$ . It would, of course, require much more work than the limited time at our disposal has permitted to establish the correctness of either.

<sup>1</sup> This Journal, 28, 1100.

In using ferrocyanide as a reagent for volumetric analysis, it is of the utmost importance to keep all of the conditions absolutely uniform. Provided this is done the results are good, but if there is any variation they are liable to be entirely incorrect.

The following table gives the analytical results in detail :

TABLE.

| Hydrochloric acid.                            |     |               | Zinc.             | Iron.   | Zinc.             | Iron.  | Zn : Fe           |
|---|-----|---------------|-------------------|---------|-------------------|--------|-------------------|
| Excess.                                       | cc. | Temper-ature. | Grams.            | Grams.  | Atoms.            | Atoms. | :: 100 ::         |
| Fe(CN) <sub>6</sub>                           | 0   | Cold          | 0.01875           | 0.01596 | 287               | 285    | 99                |
| Fe(CN) <sub>6</sub>                           | 0   | "             | 0.04598           | 0.03878 | 702               | 692    | 98                |
| Zn  | 0   | "             | 0.03280           | 0.02866 | 501               | 511    | 102               |
| Zn  | 0   | "             | 0.04579           | 0.03831 | 700               | 684    | 98                |
| Fe(CN) <sub>6</sub>                           | 5   | "             | 0.10500           | 0.06368 | 160               | 113    | 70                |
| Fe(CN) <sub>6</sub>                           | 5   | (a)           | 0.42268           | 0.05098 | 318               | 227    | 71                |
| Fe(CN) <sub>6</sub>                           | 0   | Hot           | 0.12392           | 0.07616 | 189               | 136    | 72                |
| Fe(CN) <sub>6</sub>                           | 5   | "             | 0.11500           | 0.07575 | 176               | 135    | 76                |
| Fe(CN) <sub>6</sub>                           | ½   | Cold          | 0.11469           | 0.07367 | 175               | 131    | 75                |
| Fe(CN) <sub>6</sub>                           | ½   | "             | 0.11414           | 0.07287 | 174               | 130    | 75                |
| Bought as Zn <sub>2</sub> Fe(CN) <sub>6</sub> |     |               | 0.11053           | 0.06497 | 169               | 115    | 78                |
| Bought as Zn <sub>2</sub> Fe(CN) <sub>6</sub> |     |               | 0.11157           | 0.06508 | 170               | 116    | 67                |
|   |     |               | Manganese. Grams. |         | Manganese. Atoms. |        | Mn : Fe :: 100 :: |
| Fe(CN) <sub>6</sub>                           | 0   | Cold          | 0.03050           | 0.03330 | 556               | 594    | 107               |
| Mn  | 0   | "             | 0.51763           | 0.55500 | 941               | 991    | 105               |
| Fe(CN) <sub>6</sub>                           | 5   | "             | 0.08522           | 0.06540 | 155               | 116    | 75                |
| Fe(CN) <sub>6</sub>                           | 5   | (b)           | 0.03408           | 0.05252 | 309               | 233    | 75                |
| Fe(CN) <sub>6</sub>                           | 5   | Hot           | 0.08139           | 0.09010 | 148               | 161    | 109               |
| Fe(CN) <sub>6</sub>                           | 0   | "             | 0.07938           | 0.07547 | 144               | 135    | 94                |
| Fe(CN) <sub>6</sub>                           | ½   | Cold          | 0.07757           | 0.07844 | 141               | 140    | 99                |
| Fe(CN) <sub>6</sub>                           | ½   | "             | 0.07788           | 0.07862 | 142               | 140    | 99                |

(a) Zinc and iron determined in different portions.

(b) Manganese and iron determined in different portions.

[CONTRIBUTION FROM THE ANALYTICAL LABORATORIES OF COLUMBIA UNIVERSITY.]

ON THE FERROCYANIDES OF ZINC AND MANGANESE.<sup>1</sup>

BY EDMUND H. MILLER AND J. A. MATHEWS.

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INTRODUCTION.

THE work to be described was undertaken to determine whether the precipitates formed by adding potassium ferrocyanide to solutions of zinc or manganese are normal ferrocyanides, as given by many authorities, or double potassium ferro-

<sup>1</sup> Read at the meeting of the New York Section, May 7, 1897.

cyanides, as suggested in a preliminary article which appeared in this Journal last December, and also whether the composition of the precipitate is the same if an excess of precipitant be added. The delays encountered in the course of the work made it necessary to confine ourselves to the precipitates formed in the cold, in solutions slightly acidified with hydrochloric acid, as these seemed the most important conditions on account of the solubility of the manganese ferrocyanide in hot solutions, and also on account of the zinc; for if we can establish the composition of the precipitate when formed in the cold to be  $K_2Zn$ ,  $(Fe(CN)_6)$ , we have the results of the standardizing of thousands of ferrocyanide solutions to prove it the same when hot.

*Preparation of the Ferrocyanides.*—A strong solution of zinc chloride was prepared by dissolving pure granulated zinc in hydrochloric acid, so that but a slight excess of acid remained; this was diluted and placed in two large bottles. To one portion potassium ferrocyanide was added so as to leave the zinc in excess. This was thoroughly mixed, and the presence of an excess of zinc chloride confirmed by testing with ferric chloride. The precipitate was white, flocculent, and showed at first a tendency to settle. It was washed by decantation with water seven times, the clear supernatant liquid being removed by a siphon and the precipitate thoroughly agitated with the water added. After the seventh washing no chlorides were present. The precipitate was then transferred to a filter, washed again, and then dried at  $95^{\circ} C.$  (Sample *A.*)

To the second portion an excess of potassium ferrocyanide was added and the solutions thoroughly mixed. An excess of ferrocyanide was found to be present by testing with ferric chloride. The precipitate was white, flocculent, and settled well at first, but after washing settled more slowly. It was washed six times, as already described, except that after several washings alcohol was added with the water to hasten the settling of the precipitate. This aided somewhat, but the process is not rapid, as the washing of this precipitate required eight weeks. After the sixth washing the liquid gave no test for ferrocyanide. It was not found possible to filter this zinc ferrocyanide, so it was left in the bottle and samples taken direct for the determination of the ratio of zinc to iron. (Sample *B.*)

Manganese ferrocyanides were prepared as follows : To a concentrated aqueous solution of manganeseous chloride, acidified with hydrochloric acid, potassium ferrocyanide was added so as to leave the manganese in excess. The precipitate was greenish white and flocculent, but settled slowly. It was washed with water several times, as already described. At first the precipitate ran through the filter paper, but on standing for several weeks it became more flocculent and filtered well. After filtering it was dried in an air-bath below  $100^{\circ}\text{C}$ . This ferrocyanide, when dried, has a slate color. (Sample *C*.)

Another portion of manganeseous chloride was mixed with an excess of ferrocyanide solution and allowed to stand. The precipitate scarcely settled at all, so after waiting several weeks and making several incomplete decantations, alcohol was added with the water which effected a more rapid separation. It was washed seven times ; the last wash water was free from ferrocyanide, but contained a trace of chloride. The washing of this precipitate required many weeks. (Sample *D*.) This sample was not dried but kept for the determination of ratios only. On boiling a portion of this ferrocyanide it became dark blue and more flocculent, evidently undergoing decomposition. The hydrochloric acid present in each case was about one cc. of 1.20 sp. gr. The temperature was  $23^{\circ}\text{C}$ .

These ferrocyanides have a most remarkable affinity for water. Attempts were made to determine the water present in Sample *C* by drying it in an air-bath. Eleven weighings were made at intervals of from one to two hours, at increasing temperatures from  $102^{\circ}\text{C}$ . to  $150^{\circ}\text{C}$ ., but no constant weight was reached. On cooling, water was again absorbed. The avidity for moisture is so great that the tube containing the precipitate, though tightly corked, was found to steadily increase in weight. When water is added to these ferrocyanides, dried at  $100^{\circ}\text{C}$ ., it is taken up with a crackling sound and a marked evolution of heat.

To avoid error from the absorption of moisture the following method was adopted : The tube containing the sample dried at  $100^{\circ}\text{C}$ . was weighed, then a portion shaken out into a platinum boat and the tube recorked, allowed to assume a constant weight, and reweighed. The boat containing the sample was imme-

diately placed in a glass tube in a combustion furnace, heated in a current of dry air till the sample began to char; and the water absorbed by calcium chloride. While this determination was in progress five or six portions for analysis were weighed out into small beakers by difference, then another portion was weighed into a boat as before and the moisture again determined. The average of the two percentages of moisture was used in calculating the intermediate portions to the dry basis. The percentages so obtained never varied more than one-quarter of a per cent.

Sample *A*.—Zinc chloride in excess contained: water 9.41 and 9.33 per cent., average used 9.37 per cent.

Sample *C*.—Manganous chloride in excess contained: water 3.35 and 3.11 per cent, average 3.23 per cent. Other determinations made after redrying at 100° C., after an interval of about one month, gave water 3.50 and 3.32 per cent., average 3.41 per cent., showing that the sample when dried at 100° C. has a nearly constant amount of water.

Wyruboff<sup>1</sup> assigns to the manganese ferrocyanide four molecules of water, corresponding to 2.28 per cent. We have found that, when dried from 145° to 148° C., from 2.26 to 2.36 per cent. loss in weight results, but do not believe the compound contained any definite water of crystallization. He gives to the zinc ferrocyanide twelve molecules of water, or 13.40 per cent. This result we have not confirmed.

We do not believe any further evidence is necessary to prove that these ferrocyanides are without water of crystallization.

*Methods of Decomposition.*—The ignition method given by Wyruboff was tried in connection with the determination of potash, but the results were found to be low and irregular as the resulting oxides adhered to the platinum and the potash could not be leached out completely.

Rose's method for the determination of cyanogen, as given by Fresenius, was tried on the zinc ferrocyanide but without satisfactory results. Three portions were digested with silver nitrate, adding a few drops of nitric acid from time to time, and the resulting silver cyanide weighed on balanced filters. The percentages of cyanogen were: 44.63, 44.83, and 44.12, which

<sup>1</sup> Ann. phys. Chem. (5), 8, 474, 485.

agreed well with the calculated percentages of  $Zn_2K_2(Fe(CN)_6)$ , which is 44.70, but it was found that the iron in the filtrate was invariably low and that when the precipitate of silver cyanide was scorified with test lead and cupelled, the silver resulting corresponded to only about 35 per cent. of cyanogen, showing an incomplete decomposition of the ferrocyanide.

Decomposition by means of concentrated sulphuric acid was tried with satisfactory results, except for the separation of small quantities of carbon, which had a tendency to climb up the sides of the casserole.

The method finally adopted, and which we consider entirely satisfactory, is as follows: Add to the casserole containing about one gram of the ferrocyanide, ten to fifteen cc. of concentrated nitric acid, and heat till the action is over and no more nitrous fumes are seen; cool, rinse down the sides of the casserole with water, add about twenty cc. of concentrated sulphuric acid, and boil, holding the casserole over the flame and, keeping the contents constantly in motion, until copious fumes of sulphuric acid are evolved, cool, and again rinse down the sides. At this point a decided blue color usually appears as some of the ferrocyanide which adheres to the sides of the vessel escapes decomposition; add more sulphuric acid and repeat the operation till nearly all of the sulphuric acid has been driven off; cool, dilute again, and, if no blue color appears, add a few drops of hydrochloric acid to dissolve the ferric sulphate and the solution is ready for analysis. The addition of nitric acid prevents any separation of carbon. In spite of these precautions, however, we have sometimes found traces of iron in the ferrous condition which required subsequent oxidation.

#### ANALYSIS OF THE ZINC FERROCYANIDES.

*Sample A.*—Zinc chloride in excess. Determination of zinc and iron. 0.9322 gram of the precipitate dried at 100° C. was decomposed, as already described; the iron was precipitated as basic acetate, washed, then the precipitate dissolved in hydrochloric acid and twice precipitated by ammonia. The precipitate of ferric hydroxide was dissolved in hydrochloric acid, reduced by stannous chloride, and titrated by potassium permanganate according to the Zimmerman-Reinhart method. The filtrates containing zinc were combined, acidified with acetic acid, and

the zinc precipitated as sulphide in a hot solution. The zinc sulphide, after washing, was dissolved in nitric acid, a decided excess of a saturated solution of microcosmic salt added, the solution boiled and then neutralized with ammonia, and allowed to stand on a water-bath till only a trace of ammonia remained; when cold the zinc ammonium phosphate was filtered and weighed on balanced papers after drying at 100° C. The results were: iron 16.11 per cent., zinc 27.93 per cent. A duplicate determination of iron gave 16.07 per cent.

The zinc was also determined by decomposing the ferrocyanide by potassium hydroxide, then precipitating by hydrogen sulphide, and finally, as zinc ammonium sulphate. The method gave 27.60 per cent. of zinc.

For the determination of potassium 0.5360 gram was decomposed as usual, the iron precipitated by ammonia, then the zinc by hydrogen sulphide, the filtrate acidified with sulphuric acid, and evaporated to dryness and ignited in a platinum dish. The potassium sulphate weighed 0.1208 gram, corresponding to 11.14 per cent. of potash when calculated to the dry basis.

*Sample B.*—Ferrocyanide in excess. On account of the difficulty of filtering and because the presence of potassium is already proved, only the ratio of iron to zinc was determined in this case. Portions, judged to contain about one gram of the dry compound, were transferred to casseroles as before and the alcohol driven off on the water-bath. The sample was then decomposed as usual and the zinc determined as already described. The iron was weighed as  $\text{Fe}_2\text{O}_3$ . The results were as follows:

|                    |            |
|--------------------|------------|
| Iron to zinc ..... | I : I.4000 |
| " " "              | I : I.4088 |
| " " "              | I : I.3903 |
| Average .....      | I : I.3997 |

The following table shows a comparison of our results with the theory calculated for  $\text{Zn}_2\text{K}_2(\text{Fe}(\text{CN})_6)$ , and with the analytical results of Wyruboff. The percentages of cyanogen are calculated from the iron:

|                 | Miller and Mathews. | Wyruboff. | Theory.   |
|-----------------|---------------------|-----------|-----------|
|                 | Per cent.           | Per cent. | Per cent. |
| Cyanogen.....   | 44.87               | 44.75     | 44.70     |
| Iron .....      | 16.11               | 16.07     | 16.02     |
| Zinc .....      | 27.93               | 27.60     | 28.07     |
| Potassium ..... | 11.14               | ....      | 11.20     |
|                 | —                   | —         | —         |
|                 | 100.05              | 101.82    | 99.99     |

Our results agree very closely with the theory and agree perfectly with the results obtained by titration when uranium acetate is used as an indicator. The ratio of iron to zinc is 1:1.49, compared to the theory 1:1.500, while Wyruboff's is 1:1.395. This ratio coincides almost exactly with the proportions we found when the ferrocyanide was in excess (Sample *B*), and shows that Wyruboff came to the conclusion that the precipitate was the same whichever was in excess on account of the inaccuracy of his analytical results.

The ratios obtained from Sample *B*, ferrocyanide in excess, correspond to a formula containing 5 iron and 7 zinc, which would be  $\text{Zn}_5\text{K}_4(\text{Fe}(\text{CN})_6)_2$ .

#### COMPARISON OF RESULTS.

|                                       |            |
|---------------------------------------|------------|
| Theory, iron to zinc .....            | 1 : 1.4000 |
| Miller and Mathews, iron to zinc .... | 1 : 1.3997 |
| Wyruboff, iron to zinc.....           | 1 : 1.3955 |

#### ANALYSIS OF THE MANGANESE FERROCYANIDE.

*Sample C.*—Manganous chloride in excess. Portions of about one gram each were decomposed by nitric and sulphuric acids, in the same way as the zinc ferrocyanide, then dissolved in hydrochloric acid and water, as before. The manganese and iron were determined in the same portion as follows: The iron was precipitated twice as basic acetate, then by ammonia, and weighed as  $\text{Fe}_2\text{O}_3$ . The filtrates and washings from the two basic acetate precipitations were combined, concentrated, and the manganese precipitated by bromine after adding sodium acetate, etc.; the oxide of manganese,  $\text{MnO}_2$ , was dissolved in hydrochloric and sulphurous acids, and precipitated as manganese ammonium phosphate in the ordinary manner. The manganese was ignited and weighed as pyrophosphate.

The method used for the determination of potassium was the

same as described under zinc except that the manganese was precipitated in an ammoniacal, not an acetic acid solution.

The results calculated to the dry basis are as follows : Iron 16.36 and 16.40 per cent., manganese 17.67 and 17.67 per cent., potassium 20.33 and 19.64 per cent.

Other determinations of manganese and iron in the same portion gave the following ratios :

$$\text{Fe} : \text{Mn} :: 1 : 1.1039, \text{ and as } 1 : 1.1080$$

*Sample D.*—Ferrocyanide in excess. On account of the perverse character of this precipitate only the ratio of iron to manganese was determined. The method of decomposition and analysis has already been described. The results are as follows :

$$\text{Fe} : \text{Mn} :: 1 : 1.0502$$

$$\text{Fe} : \text{Mn} :: 1 : 1.0623$$

$$\text{Fe} : \text{Mn} :: 1 : 1.0758$$

The following table gives a comparison of our results with the theory calculated from Wyrouboff's formula without the water of crystallization,  $5\text{Mn}_2\text{Fe}(\text{CN})_6$ ,  $4\text{K}_2\text{Fe}(\text{CN})_6$ , and with his own results. The cyanogen is calculated from the iron :

|                | Miller and Mathews.<br>Per cent. | Wyrouboff.<br>Per cent. | Theory.<br>Per cent. |
|----------------|----------------------------------|-------------------------|----------------------|
| Cyanogen ..... | 45.57                            | 45.68                   | 45.44                |
| Iron .....     | 16.36                            | 16.40                   | 16.31                |
| Manganese..... | 17.67                            | 17.67                   | 18.19                |
| Potassium..... | 20.33                            | ....                    | 19.35                |
|                | 99.93                            | 99.29                   | 99.98                |

These results agree very fairly with the theory for Wyrouboff's formula, but still better with a ratio of 10 iron to 11 manganese, as will be seen from the following ratios :

$$\text{Fe} : \text{Mn} :: 1 : 1.099$$

$$\text{Fe} : \text{Mn} :: 1 : 1.097$$

$$\text{Fe} : \text{Mn} :: 1 : 1.104$$

$$\text{Fe} : \text{Mn} :: 1 : 1.108$$

$$\text{Average } 1 : 1.102$$

$$\text{Theory for 10 Fe : 11 Mn, } 1 : 1.100$$

While these results agree most perfectly with a ratio of 10 to

11, we do not wish to advance a corresponding formula, as the difference between this ratio and the 9 to 10 of Wyrouboff is very slight and the composition of the precipitate very readily affected by slight changes in the conditions of precipitation. The average of three ratios of iron to manganese determined on Sample *D*, ferrocyanide in excess, is 1 : 1.0628, corresponding to a formula containing 16 iron to 17 manganese. We do not give to this ratio its appropriate formula, as the precipitate may be a mixture of two simple ferrocyanides, but we believe that a comparison of these ratios shows that the manganese precipitate does not have the same composition whether manganese or ferrocyanide is in excess, as stated by Wyrouboff.

The physical properties of this precipitate confirm the fact that it readily undergoes a change in composition, for if a solution of potassium ferrocyanide is poured into one of manganous chloride it first is pinkish white, on adding more ferrocyanide it becomes greenish, and when the ferrocyanide is in excess a light slate color.

The conclusions arrived at by us are :

*First.*—The precipitates formed by potassium ferrocyanide and chloride of zinc or manganese are double ferrocyanides and not normal ferrocyanides, as given by Prescott and Johnson<sup>1</sup> and by Stone.<sup>2</sup>

*Second.*—The ferrocyanides formed when the metal is in excess does not contain water of crystallization, as given by Wyrouboff.<sup>3</sup>

*Third.*—The precipitate formed in a dilute hydrochloric acid solution of zinc chloride by potassium ferrocyanide when the zinc chloride is in excess, is  $Zn, K, (Fe(CN)_6)$ , as given by Wyrouboff.<sup>3</sup>

The precipitate is not the same whichever is in excess. When ferrocyanide is in excess the ratio of iron to zinc is as 1 to 1.40, which corresponds to  $Zn, K, (Fe(CN)_6)$ .

*Fourth.*—The manganese precipitate formed when manganese chloride is in excess agrees well with the formula  $5Mn, Fe(CN)_6, 4K, Fe(CN)_6$ , as given by Wyrouboff, but better with a ratio of 10 iron to 11 manganese. When the ferrocyanide is in excess the

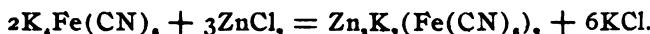
<sup>1</sup> Qual. Anal., pp. 57 and 67.

<sup>2</sup> This Journal, 17, 473.

<sup>3</sup> Am. Chim. Phys. (5), 8, 474, 485.

composition is different, corresponding to a ratio of 16 iron to 17 manganese. The manganese precipitate is very readily affected by changes in the conditions of precipitation.

In regard to the bearing of these results on the methods in use for the titration of zinc and manganese by potassium ferrocyanide, we believe the accuracy of the ordinary method of titrating zinc in a dilute hydrochloric acid to be confirmed and that the following reaction takes place :



The difference in the composition of the precipitate when ferrocyanide is in excess explains why all attempts to add an excess of ferrocyanide and titrate back by permanganate have failed.

The complicated and variable character of the manganese precipitate constitutes a serious objection to the method of determining manganese by potassium ferrocyanide, for aside from the difficulties arising from the solubility of the manganous ferrocyanide and its consequent action on indicators, the titration must be conducted under very carefully regulated conditions to give satisfactory results.

#### DISCUSSION ON THIS AND THE PRECEDING PAPER.<sup>1</sup>

*Mr. Miller:* All of these ferrocyanides can be resolved into two ferrocyanides having simple ratios, as follows :

Zinc in excess :



$\text{K}_4\text{Fe}(\text{CN})_6$ , in excess :



Manganese in excess :



$\text{K}_4\text{Fe}(\text{CN})_6$ , in excess :



The explanation may be as follows : The acid in solution (HCl) reacting on the potassium ferrocyanide gives free hydro-

<sup>1</sup> NOTE BY THE EDITOR.—The Publication Committee have decided to publish the discussion on this and the preceding paper inasmuch as it seems to throw some additional light upon the subject. Hereafter such discussions, if published, will appear in the Proceedings.

ferrocyanic acid, which precipitates the normal ferrocyanide,<sup>1</sup> liberating in turn free acid, which continues the reaction. In this way a little acid can effect a great change in the composition of the precipitate.

If this theory is correct in a neutral solution,  $ZnK_2Fe(CN)_6$ , and  $MnK_2Fe(CN)_6$ , should be formed, while the proportions of zinc or manganese to potassium ferrocyanide remaining the same the greater the quantity of acid the more of the normal ferrocyanide  $R_2Fe(CN)_6$ , should be formed. This may be complicated, however, by the solubility of the manganese compound.

Expressed briefly, as the acid increases, the manganese or zinc in the ratio increases, and as the ferrocyanide increases, the zinc or manganese in the ratio diminishes.

This view of the composition and conditions for formation of these precipitates has received most important confirmation from the work of Stone and Van Ingen, for as I had expected they have found the two salts,  $K_2MnFe(CN)_6$ , and  $K_2ZnFe(CN)_6$ , to be formed in a cold neutral solution. The compound  $K_2Mn_2(Fe(CN))_6$ , and  $K_2Zn_2(Fe(CN))_6$ , also agree with this theory, for they may be resolved into  $R_2Fe(CN)_6 \cdot 2K_2RFe(CN)_6$ , and are formed in an exceedingly dilute acid solution and occupy a position intermediate between the  $K_2ZnFe(CN)_6$ , of the neutral solution, and the  $Zn_2Fe(CN)_6 \cdot K_2ZnFe(CN)_6$ , obtained when more hydrochloric acid is present.

It must be admitted that these precipitates are extremely sensitive to changes of condition, but we have in uranium acetate an indicator which in an acid solution shows with certainty  $Zn_2K_2Fe(CN)_6$ , and according to Stone and Van Ingen we have in dilute cobalt nitrate an indicator which turns at  $K_2R_2(Fe(CN))_6$ .

*Mr. Van Ingen:* I know that in carrying out the work of Mr. Stone, in obtaining a precipitate for analysis, there were two or three cases in which decomposition took place, and we had a ferrocyanide of iron formed, not shown by the strong blue color in the precipitate.

Another matter: a very curious changing in color took place during the washing of the manganese precipitate where we had manganese in excess and not where we had ferrocyanide in excess. It would start out sometimes with dark purple, from dark purple

<sup>1</sup> Wyrouboff: Ann. phys. Chem. (5), 8, 474.

to a dark pink, and gradually washing out until we ended with a pale slate color, and the solubility made it very hard to know just when we got through, because the cobalt tests would show ferrocyanide to the very end. All the precipitates were washed in bulk of 6,700 cc., allowed to settle in bottles, then siphoned off as far as possible, and water added. Most of them had from twenty to thirty washings, and by adding barium chloride we were enabled to get four or five washings a day. Before doing that, we were well satisfied with one washing in two days. As you continue, the washing and settling get slower and slower, but there seems to be some very curious change in the manganese salts during this washing. The precipitate changed color in parts entirely during the washing.

*Mr. Miller*: There is a difference in color where the manganese or ferrocyanide is in excess and you get changes in color going from one washing to another.

*Mr. Van Ingen*: I was referring to washing the precipitate where manganese was in excess. We started with pinkish purple and ended up with a slate color.

*Mr. Miller*: I don't remember seeing a purple color, but I noticed a change from pinkish to sort of slate color.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

### HALIDES AND PERHALIDES OF PYRIDINE.<sup>1</sup>

By P. F. TROWBRIDGE AND O. C. DIEHL.

Received May 21, 1897.

#### ACTION OF BROMINE UPON IODIDES OF PYRIDINE.

*Pyridine Hydriodide Dibromide*,  $C_6H_5N\cdot HI\cdot Br_2$ , or  $C_6H_5N\cdot HBr\cdot IBr$ .—Reddish-brown, thin laminae or large, prismatic plates. Melting-point  $172^{\circ}$ - $175^{\circ}$  C. Very soluble in alcohol, with difficulty in chloroform, and scarcely at all in water. The samples for analysis were crystallized from alcohol.

Pure pyridine hydriodide was dissolved in water and brominated by passing carbon dioxide through bromine and then through the solution. At first a very dark red precipitate formed which appeared to be nearly pure iodine. Upon continued bromination the precipitate became brownish yellow,

<sup>1</sup> Continuation of previous paper. This Journal, 19, 322.

flocculent, and readily floated in the liquid. Gradually the precipitate became heavier and finally settled as a dark brown, viscous mass. A small amount of heat was generated during the bromination. Upon standing the precipitate became crystalline and the solution showed the presence of some iodine. The pure product was obtained by several crystallizations from alcohol.

|                        | Calculated for<br>$C_6H_5N \cdot HI \cdot Br_2$ . | Found. |       |
|------------------------|---|--------|-------|
|                        | I.  | II.    |       |
| Titrated halogen ..... | 43.59   | 43.47  | 43.03 |
|                        |   | 43.41  |       |
| Total halogen.....     | 78.01   | 77.82  | ....  |
|                        |   | 78.12  |       |

*Pyridine Methyl Iodide Dibromide*,  $C_6H_5N \cdot CH_3I \cdot Br_2$ , or  $C_6H_5N \cdot CH_3Br \cdot IBr$ .—Bright orange-yellow crystals, soluble in alcohol and acetone, does not crystallize well from the latter, insoluble in water and ether. From an absolute alcohol solution orange-yellow, short, prismatic, needle-like crystals were obtained. Melting-point  $61^{\circ}$ - $62^{\circ}$  C.

A water solution of pure pyridine methyl iodide was brominated in the same manner as the pyridine hydriiodide. A heavy reddish brown oil formed, having a strong bromine-like odor. Potassium hydroxide decomposes the oil. When the oil is heated on the water-bath for several hours the bromine odor disappears and the oil becomes lighter in color. On cooling it forms a bright-orange crystalline mass. This was purified from alcohol.

|                          | Calculated for<br>$C_6H_5N \cdot CH_3I \cdot Br_2$ . | Found. |
|--------------------------|--|--------|
| Titrated halogen.....    | 41.96  | 41.53  |
| Total     "        ..... | 75.26  | 75.04  |

*Pyridine Ethyl Iodide Dibromide*,  $C_6H_5N \cdot C_2H_5I \cdot Br_2$ , or  $C_6H_5N \cdot C_2H_5Br \cdot IBr$ .—Orange-yellow crystals, soluble in alcohol. Melting-point  $25^{\circ}$ - $26^{\circ}$  C.

This preparation was made by aspirating air through bromine and into a water solution of pure pyridine ethyl iodide. A dark red oil formed, which was separated from the liquor (no iodine found in liquor), and heated for a time on the water-bath. The oil was then purified by dissolving in alcohol.

|                          | Calculated for<br>$C_6H_5N.C_6H_4I.Br_2$ | Found.                    |
|--------------------------|--|---------------------------|
|                          | I.                                       | II.                       |
| Titrated halogen.....    | 40.49                                    | { 40.02<br>40.26          |
| Total     "        ..... | 72.59                                    | 40.34<br>72.34      72.89 |

## ACTION OF CHLORINE UPON IODIDES OF PYRIDINE.

Pictet and Kraft<sup>1</sup> report several mixed perhalides of pyridine, quinoline, and piperidine. By adding iodine trichloride to a water solution of pyridine hydrochloride they get pyridine hydrochloride iodine chloride,  $C_6H_5N.HCl.ICl$ . Melting-point 180°. Analysis not given. The water present decomposes the iodine trichloride according to the equation,



By treating the above hydrochloride with caustic alkali, pyridine iodine chloride is formed, white needles melting at 132° C. Close analytical results are given. They report analogous products of quinoline and piperidine. The  $C_6H_5N.HCl.ICl$ , melting at 90° C. is of especial interest as it is made by adding iodine chloride (ICl) to piperidine hydrochloride and also by adding hydrochloric acid to piperidine iodine chloride,  $C_6H_5N.ICl$ .

Dittmar<sup>2</sup> uses iodine monochloride (ICl) and obtains the same bodies as reported by Pictet and Kraft. By chlorination of  $C_6H_5N.HCl.ICl$  he obtains  $C_6H_5N.HCl.ICl_2$ . This is an unstable body and according to Pictet and Kraft cannot be made by treating the pyridine hydrochloride with iodine trichloride.

In our study we did not attempt to confirm the results just cited. Our aim was to study the effect of chlorine on pyridine derivatives containing iodine, hence we did not make use of iodides of chlorine direct.

*Pyridine Hydriodide Trichloride*,  $C_6H_5N.HI.Cl_3$ ; or  $C_6H_5N.HI.Cl_2$ ,  $C_6H_5N.HI.Cl_1$ ; or  $C_6H_5N.HCl.ICl$ ,  $C_6H_5N.HCl.ICl_2$ .—Chlorine gas was passed through a water solution of pure pyridine hydriodide to complete saturation. At first iodine is set free. It then combines with more chlorine and a bright lemon-yellow flocculent precipitate is formed. It crystallizes nicely from alcohol. Melting-point 176° C. The precipitate contains an abundance of iodine.

<sup>1</sup> Bull. Soc. Chim. [3], 7, 72.

<sup>2</sup> Ber. d. chem. Ges., 18, 1613.

|                        | Calculated for<br>$C_6H_5N.CH_2Cl_2$ . | I.    | Found.<br>II. | III.  |
|------------------------|--|-------|---------------|-------|
| Titrated halogen ..... | 33.13                                  | 33.33 | 33.17         | 33.93 |
| Total " .....          | 74.09                                  | 74.76 | 73.83         | 73.18 |

We could not by this method of simple chlorination obtain a body having four atoms of chlorine. The body we obtained consists probably of equal portions of the dichloride and tetrachloride.

*Pyridine Methyl Iodide Tetrachloride*,  $C_6H_5N.CH_2I.Cl_4$ , or  $C_6H_5N.CH_2Cl.ICl$ .—A canary-yellow powder melting at 185° C.

|                        | Calculated for<br>$C_6H_5N.CH_2I.Cl_4$ . | Found. |
|------------------------|--|--------|
| Titrated halogen ..... | 39.17                                    | 39.16  |

Made by passing chlorine into a water solution of pyridine methyl iodide to saturation.

Bally<sup>1</sup> reports the same body,  $C_6H_5N.CH_2Cl.ICl$ , by passing chlorine into a mixture of  $C_6H_5N.CH_2Cl$  and potassium hydroxide. He then acidifies and obtains a yellow body which melts at 179°–180° C. He makes  $C_6H_5N.CH_2Cl.ICl$  by treating  $C_6H_5N.CH_2I$  with chlorine. Melting-point 90° C.

Ostermayer<sup>2</sup> reports this last body,  $C_6H_5N.CH_2Cl.ICl$ , but with a melting-point of 81°–82° C., by treating  $C_6H_5N.CH_2Cl$  with iodine chloride (ICl). The iodine chloride is made by passing chlorine into iodine suspended in water.

*Pyridine Ethyl Iodide Tetrachloride*,  $C_6H_5N.C_2H_5I.Cl_4$ , or  $C_6H_5N.C_2H_5Cl.ICl$ .—Made by passing chlorine through a water solution of pyridine ethyl iodide. At first iodine is thrown out of solution. Gradually the solution assumes a lighter color, the iodine disappears, and finally a canary-yellow precipitate is obtained. Melting-point 123° C.

|                        | Calculated for<br>$C_6H_5N.C_2H_5I.Cl_4$ . | Found. |
|------------------------|--|--------|
| Titrated halogen ..... | 37.71                                      | 37.43  |
| Total " .....          | 71.28                                      | 71.16  |

#### ACTION OF BROMINE UPON PYRIDINE.

Anderson<sup>3</sup> treats a water solution of pyridine with bromine water and reports (no analysis given) an addition product with probably more than one atom of bromine. He also treats dry

<sup>1</sup> *Ber. d. chem. Ges.*, 21, 1772.

<sup>2</sup> *Ibid.*, 18, 591.

<sup>3</sup> *Ann. Chem. (Liebig)*, 105, 341.

pyridine with dry bromine and reports pyridine hydrobromide as one of the products formed (no analysis given).

Hofmann<sup>1</sup> treats pyridine hydrochloride with bromine and gets a body which he does not analyze but erroneously assumes to have the formula  $C_5H_4NBr_4$ . More is given in this paper concerning this product under "Action of Bromine upon Chlorides of Pyridine."

Grimaux<sup>2</sup> treats pyridine with three times its volume of bromine and obtains an unstable body, which he crystallizes from chloroform or alcohol. He gets thin red plates, melting at 126° C., to which he assigns the formula  $(C_5H_4NBr_4)_2HBr$ . His analysis shows about two and one-half atoms of bromine to five atoms of carbon, but he does not report the action of reducing agents like sodium thiosulphate, which, if his formula be correct, would show four atoms of titrated bromine and five atoms of total bromine to ten atoms of carbon. We could not reproduce Grimaux's compound by this method. See further in this paper under "Action of Bromine upon Bromides of Pyridine."

After many ineffectual attempts to form a definite compound by the action of bromine in varying quantities upon dry pyridine and pyridine in water solution, pyridine was dissolved in a large excess of chloroform and treated with bromine vapors. A red oil separated at first which rapidly went into solution. As the solution became saturated with the bromine, fine dark red needle-like crystals separated out. These were carefully and rapidly dried and analyzed. Melting-point 58.5° C.

|                    | Calculated for<br>$C_5H_4NBr_4$ | Calculated for<br>$C_5H_4N.HBr.Br_3$ | Found.<br>I.     | Found.<br>II. |
|--------------------|---------------------------------|--------------------------------------|------------------|---------------|
| Titrated bromine.. | 80.16                           | 59.97                                | { 80.23<br>80.15 | 79.31         |
| Total        "     | .. 80.16                        | 79.96                                | { 79.30<br>79.91 | ....          |

The tetrabromide is unstable and loses bromine upon exposure, becoming lighter in color. After several days it ceases to lose bromine and becomes light yellow with a melting-point of 94°-95° C. Titration gives 66.71 per cent. of bromine; theory for  $C_5H_4N.Br_4$  gives 66.89 per cent. of bromine.

#### BROMIDES OF PYRIDINE.

*Pyridine Hydrobromide*,  $C_5H_4N.HBr$ .—Colorless transparent

<sup>1</sup> *Ber. d. chem. Ges.*, 1879, 988.

<sup>2</sup> *Compt. rend.*, 95, 85.

feathery scales, slightly deliquescent, soluble in alcohol, chloroform, and water, insoluble in ether, melts at 200° C. with decomposition. Made by neutralizing pure pyridine with hydrobromic acid and evaporating gently to crystallization.

|               | Calculated for<br>$C_6H_5N \cdot HBr$ . | Found.           |
|---------------|---|------------------|
| Bromine ..... | 49.93                                   | { 49.17<br>49.93 |

*Pyridine Methyl Bromide*,  $C_6H_5N \cdot CH_3Br, \frac{1}{2}H_2O$ .—Forms large translucent crystals from alcoholic solution, soluble in water, alcohol, and chloroform, insoluble in ether. Melts with slight decomposition at 135.5° C. Made by passing methyl bromide gas through pure pyridine cooled in salt and ice. The fine, white crystals were washed with ether and crystallized from alcohol.

|               | Calculated for<br>$C_6H_5N \cdot CH_3Br, \frac{1}{2}H_2O$ | Calculated for<br>$C_6H_5N \cdot CH_3Br$ | Found.           |
|---------------|---|--|------------------|
| Bromine ..... | 43.88   | 45.33                                    | { 44.23<br>43.72 |

We have not yet succeeded in preparing a sample that gives sufficient bromine for the pure bromide without some water of crystallization.

*Pyridine Ethyl Bromide*,  $C_6H_5N \cdot C_2H_5Br$ .—White crystals melting at 111°–112° C., soluble in alcohol and water, insoluble in ether. Made by adding ethyl bromide to pure pyridine. At ordinary temperature the action is very slow and almost no heat is generated. When the mixture is warmed a violent action takes place with the generation of heat. An excess of ethyl bromide should be used and the flask provided with a reflux condenser. After the reaction has ceased (one-half hour) the ethyl bromide may be distilled off before crystallization from alcohol.

|               | Calculated for<br>$C_6H_5N \cdot C_2H_5Br$ | Found.           |
|---------------|--|------------------|
| Bromine ..... | 42.49                                      | { 41.82<br>41.88 |

#### ACTION OF IODINE UPON BROMIDES OF PYRIDINE.

*Pyridine Hydriodide Periodide*,  $C_6H_5N \cdot HI \cdot I^1$ .—Iodine in alcoholic or potassium iodide solution displaces bromine in pyridine hydrobromide. The particular periodide formed depends upon temperature of experiment and amount of iodine used. When

<sup>1</sup> This Journal, 19, 327.

the crystals obtained are well washed with ether and recrystallized from alcohol, they are found to be entirely free from bromine. In this manner  $C_6H_5N.HI.I$  was obtained and also higher periodides, which were only tested to prove the absence of bromine.

*Pyridine Methyl Iodide Tetriiodide*,  $C_6H_5N.CH_3.I_4$ .<sup>1</sup>—To an aqueous solution of pyridine methyl bromide a potassium iodide solution of iodine was added. Bronze-green crystals were formed at once. These, upon purification, showed entire absence of bromine and on analysis gave good figures for  $C_6H_5N.CH_3.I_4$ . The same results were obtained using an alcoholic solution of iodine.

*Pyridine Ethyl Iodide Periodide*,  $C_6H_5N.C_2H_5.I_4$ .—On treatment of pyridine ethyl bromide with alcoholic or with potassium iodide solution of iodine, an oil was obtained entirely free from bromine. This body could not be obtained in a crystalline condition. Analysis gives figures too high for the triiodide,  $C_6H_5N.C_2H_5.I_3$ ,<sup>2</sup> which melts at 51° C. This is probably the pentiodide,  $C_6H_5N.C_2H_5.I_5$ , not entirely pure.

#### ACTION OF BROMINE UPON BROMIDES OF PYRIDINE.

*Pyridine Hydrobromide Perbromide*,  $(C_6H_5N.HBr)_2Br_2$ , or  $C_6H_5N.HBr.Br.C_6H_5N.HBr.Br_2$ .—Very stable, dark orange-colored prismatic crystals. Melting-point 125° C. Made by aspirating bromine through a water solution of pyridine hydrobromide until the orange crystals which first formed were dissolved in the excess of bromine. The oil was separated and became a crystalline solid upon exposure for the evaporation of the excess of bromine. This solid was heated on the water-bath for some time and then crystallized from alcohol.

|                   | Theory for<br>$(C_6H_5N.HBr)_2Br_2$ . | Theory for<br>$C_6H_5N.HBr.Br.C_6H_5N.HBr.Br_2$ . | Theory for<br>$C_6H_5N.HBr.Br_2$ . | Found. |
|-------------------|---------------------------------------|---|------------------------------------|--------|
| Titrated bromine. | 42.82                                 | 33.30   | 51.58                              | 41.95  |
| Total             | " . 71.37                             | 66.61   | 74.95                              | 70.86  |

It is very probable that this is the same body reported by Grimaux<sup>3</sup> and referred to in this paper under "Action of Bromine upon Pyridine." However, he reports his product unstable, melting at 126° C. The body we obtain is perfectly stable, does

<sup>1</sup> This Journal, 19, 324.

<sup>2</sup> This Journal, 19, 329.

<sup>3</sup> Compt. rend., 95, 85.

not give off bromine when heated on the water-bath and melts at 125° C. Grimaux assigns the formula  $(C_6H_5NBr_2)_2HBr$ , which differs from our formula in total amounts of the elements by one hydrogen atom, but differs widely in the structural relation. The total bromine and the combustion would give the same results for both formulas. Total bromine for Grimaux 71.50 per cent. According to his formula four atoms of the bromine are *per halogen* and should react with sodium thiosulphate, giving 57.38 per cent. of titrated bromine. Our formula calls for 42.85 per cent. of titrated bromine, which is confirmed by the analysis. This body is then a mixture of one molecule each of the mono- and dibromide of pyridine hydrobromide, and not the monohydrobromide of two molecules of pyridine dibromide.

By checking the bromination of the pyridine hydrobromide at the formation of the first crystals a lighter orange-colored body is obtained, which crystallizes nicely from alcohol and is perfectly stable. Melting-point 93° C.

|                        | Calculated for<br>$C_6H_5N.CH_2Br.Br$ . | Found. |
|------------------------|---|--------|
| Titrated bromine ..... | 33.30                                   | 32.66  |

*Pyridine Methyl Bromide Dibromide*,  $C_6H_5N.CH_2Br.Br_2$ .—A dark orange-red crystalline body. Melting-point 66° C. Soluble in alcohol and acetic ether, insoluble in carbon bisulphide, chloroform, water, and ether. It is decomposed by acetone. Made by aspirating bromine through a water solution of pyridine methyl bromide. The excess of bromine was driven off on the water-bath and the crystalline mass further purified by recrystallization from alcohol.

|                          | Calculated for<br>$C_6H_5N.CH_2Br.Br_2$ . | I.    | II.   |
|--------------------------|---|-------|-------|
| Titrated bromine .. .... | 47.87                                     | 48.03 | 48.08 |
| Total " .. ....          | 71.80                                     | 71.74 | 71.60 |

Ostermayer<sup>1</sup> treats pyridine methyl chloride with bromine and obtains a body melting at 48° C., which loses bromine in the air. He assigns the formula  $C_6H_5N.CH_2Br.Br_2$ , but reports no analysis.

*Pyridine Ethyl Bromide Dibromide*,  $C_6H_5N.C_2H_5Br.Br_2$ .—The same in appearance and properties as the methyl compound just

<sup>1</sup> Ber. d. chem. Ges., 18, 599.

described, and made in the same manner. Melting-point 35° C.

|                           | Calculated for<br>$C_6H_5N.C_6H_5Br.Br_2$ . | Found. |
|---------------------------|---|--------|
|                           | I.  | II.    |
| Titrated bromine.....     | 45.94                                       | 45.55  |
| Total      "        ..... | 68.91                                       | 68.90  |

#### ACTION OF CHLORINE UPON THE BROMIDES OF PYRIDINE.

*Pyridine Hydrobromide Perchloride* (?).—When chlorine is passed into a water solution of pyridine hydrobromide, some bromine is evolved and a reddish-yellow crystalline precipitate is formed. This precipitate becomes a yellow oil upon complete saturation with chlorine. Upon exposure or warming on the bath this becomes solid. Qualitative tests show an abundance of bromine and chlorine. The yellow crystals assume a reddish tinge when washed with water; this disappears if the crystals are then washed with ether. The compound is not stable; chlorine is evolved on standing, and possibly some bromine, although the bromine odor was not observed. This preparation was made several times, giving to all appearances exactly the same body, and having approximately the same melting-point, 51° C. Analysis, however, shows widely different results. It seems quite probable that  $C_6H_5N.HCl.BrCl$  is formed, but in all cases impure, owing to the volatilization of some of the bromine as soon as it is set free by the chlorine and before it can enter into combination with more chlorine. Samples IV and V were given an extra long treatment with chlorine.

|                           | Calculated for<br>$C_6H_5N.HBr.Cl$ . | Calculated for<br>$C_6H_5N.HCl.BrCl$ . | Found.                         |                                |                                |
|---------------------------|--------------------------------------|--|--------------------------------|--------------------------------|--------------------------------|
|                           | I.                                   | II.                                    | III.                           | IV.                            | V.                             |
| Titrated halogen 18.17    | 30.68                                | { 25.59<br>25.28                       | 15.63<br>14.72                 | 13.48<br>13.30                 | 16.93<br>16.75                 |
|                           |                                      | { 24.16<br>25.12<br>23.60<br>23.29     | 14.79<br>....<br>13.22<br>.... | 13.62<br>....<br>11.90<br>.... | 16.85<br>16.62<br>....<br>.... |
| Total      "        59.01 | 65.29                                | { 57.30<br>57.46                       | ....                           | 53.04<br>54.89                 | 65.02<br>65.82                 |
|                           |                                      |  |                                | 63.69                          | 62.41                          |

*Pyridine Methyl Bromide Dichloride*,  $C_6H_5N.CH_3Br.Cl_2$ , or  $C_6H_5N.CH_3Cl.BrCl$ .—When pyridine methyl bromide in water solution is treated with chlorine some bromine escapes and a light yellow precipitate forms, becoming a red oil upon complete saturation with chlorine. This body is not stable, but upon standing or gently warming loses most of its halogen odor and becomes solid at about 19° C.

|                    | Calculated for<br>$C_6H_5N.CH_3Br.Cl_2$ . | Calculated for<br>$C_6H_5N.CH_3Br.Cl$ . | Found.        |
|--------------------|---|---|---------------|
|                    | I.  | II.                                     |               |
| Titrated halogen.. | 29.00                                     | 16.90                                   | { 27.96 27.94 |
| Total " ..         | 61.56                                     | 55.06                                   | { 27.86 27.85 |
|                    |   |   | 61.00 61.12   |

*Pyridine Ethyl Bromide Dichloride*,  $C_6H_5N.C_2H_5Br.Cl_2$ , or  $C_6H_5N.C_2H_5Cl.BrCl$ .—A pale yellow precipitate is first formed, when chlorine is passed into a water solution of pyridine ethyl bromide. Some bromine escapes. This precipitate becomes a red oil upon complete saturation with chlorine. This oil could not be purified so as to obtain a crystalline body. The oil was gently warmed for some time and analyzed.

|                    | Calculated for<br>$C_6H_5N.C_2H_5Br.Cl_2$ . | Calculated for<br>$C_6H_5N.C_2H_5Br.Cl$ . | Found.        |
|--------------------|---|---|---------------|
|                    | I.  | II.                                       |               |
| Titrated halogen.. | 27.43                                       | 15.84                                     | { 27.19 27.77 |
| Total " ..         | 57.49                                       | 51.60                                     | { 26.13 27.81 |
|                    |   |   | 55.15 55.75   |

#### ACTION OF CHLORINE UPON PYRIDINE.

Anderson<sup>1</sup> treats pyridine with chlorine and gets pyridine hydrochloride and a white product having the hypochlorite odor. No analysis reported.

Kaiser<sup>2</sup> treats pure pyridine with dry chlorine and obtains ultimately a hydrochloride of dichloropyridine,  $C_6H_5Cl_2N.HCl$ , a substituted body and pyridine chloride,  $C_6H_5N.Cl$ , an addition body. He also treats pyridine dissolved in water with chlorine gas and obtains an addition-product having a chloride of lime odor. He concludes that this is pyridine hypochlorite,  $C_6H_5N.HOCl$ . Upon passing more chlorine into this product pyridine is decomposed with evolution of carbon dioxide, nitrogen, etc. When he treats pyridine and potassium hydroxide with chlorine, chloroform, dichloracetic acid, carbon dioxide, and nitrogen are formed.

We treated a chloroform solution of pyridine with dry chlorine to complete saturation. A few oily drops formed at the first which almost immediately went into solution, and no further change was noticed during the long-continued chlorination. The solution was then gently evaporated to expel the excess of chlorine and the chloroform. A brownish colored oil was left behind which did not solidify upon standing. On addition of a

<sup>1</sup> Ann. Chem. (Liebig), 105, 340.

<sup>2</sup> Am. Chem. J., 8, 312.

few drops of water the oil becomes a white flocculent powder, which does not dissolve in great excess of water. This oil has an odor somewhat like chloride of lime. When a crystal of potassium iodide is added to the oil no iodine is set free, nor when to this water and hydrochloric acid are added. Iodine is not set free when potassium iodide is added to the oil after the addition of water. This seems to be conclusive proof that the body is not a hypochlorite or a perchloride of pyridine. We hope later to investigate this body more fully.

#### CHLORIDES OF PYRIDINE.

*Pyridine Hydrochloride*,  $C_5H_5N \cdot HCl$ .—Transparent, colorless crystals, soluble in alcohol, chloroform, hydrochloric acid, and water; insoluble in ether, and is thrown down from its alcoholic solution by the addition of ether. It crystallizes in scales from a solution in absolute alcohol. It cannot be crystallized from its water solution. It is made by adding concentrated hydrochloric acid in excess to pure pyridine. The solution is heated on the bath and then cooled over sulphuric acid. The salt separates out as a mass of thin scales, which are purified by recrystallization from absolute alcohol. Melting-point  $82^\circ C.$ <sup>1</sup>

|               | Calculated for<br>$C_5H_5N \cdot HCl$ . | Found.           |
|---------------|---|------------------|
| Chlorine..... | 30.73                                   | { 30.23<br>30.28 |

*Pyridine Methyl Chloride*,  $C_5H_5N \cdot CH_3Cl$ .—Ostermayer<sup>2</sup> has reported the formation of this salt by heating pyridine, hydrochloric acid, and methyl alcohol to  $230^\circ C.$  for ten hours. He fails to obtain stable crystals but proves the purity of his syrupy solution by the formation and analysis of the gold and platinum double salts.

Lange<sup>3</sup> makes the pyridine methyl chloride by shaking the iodide with moist silver chloride. We tried to obtain the chloride in crystalline form by saturating pure pyridine with methyl chloride; failing in this we adopted the method of Lange. This

<sup>1</sup> The sample from which the melting-point was obtained was made by passing dry hydrochloric acid gas into dry pyridine cooled in ice. This was well washed with ether, and melting-point taken. This preparation distils with some decomposition. A strong odor of pyridine is observed. Voluminous white vapors are formed, which condense on the sides of the flask and thermometer, and solidify when cooled to  $118^\circ C.$

<sup>2</sup> Ber. d. chem. Ges., 18, 591.

<sup>3</sup> Ibid., 1885, 3438.

same method was used in the preparation of pyridine ethyl chloride. Whenever the pyridine methyl or ethyl chloride was desired the corresponding iodide was shaken with an excess of freshly precipitated silver chloride, till a portion of the clear liquid gave no test for iodine. The chloride was always used in solution. All attempts to obtain the crystalline body failed.

#### ACTION OF IODINE UPON CHLORIDES OF PYRIDINE.

*Pyridine Hydriodide Hexiodide*,  $C_6H_5N\cdot HI\cdot I_5$ .<sup>1</sup>—When an alcoholic solution of iodine is added to pyridine hydrochloride, the latter being in excess, a dark crystalline body is obtained which, when crystallized from alcohol, gives tests for chlorine. When an excess of alcoholic solution of iodine is added to pyridine hydrochloride the heptiodide,  $C_6H_5N\cdot HI\cdot I_6$ , fairly pure, is obtained perfectly free from chlorine after a second crystallization from alcohol. Melting-point  $71^{\circ}\text{--}72^{\circ}$  C.

*Pyridine Methyl Iodide Tetriiodide*,<sup>2</sup>  $C_6H_5N\cdot CH\cdot I\cdot I_3$ .—When an excess of alcoholic solution of iodine is added to pyridine methyl chloride, a dark green oil is at once formed. This is carefully separated and dissolved in alcohol. From this solution, after a second treatment with alcohol, fine needle-like crystals are obtained free from chlorine. Analysis shows these crystals to be the pentiodide.

*Pyridine Ethyl Iodide Periodide*,  $C_6H_5N\cdot C_2H_5\cdot I\cdot I_2$ .—When an alcoholic solution of iodine, in excess, is added to pyridine ethyl chloride, a dark green oil is formed. This is carefully separated and dissolved in alcohol and is again obtained as an oil which does not contain chlorine. All attempts to obtain a crystalline body failed, and analysis of the oil showed it to be an impure periodide, but containing more iodine than required for  $C_6H_5N\cdot C_2H_5\cdot I\cdot I_2$ , which melts at  $51^{\circ}$  C.<sup>3</sup>

#### ACTION OF BROMINE UPON CHLORIDES OF PYRIDINE.

*Pyridine Hydrobromide Dibromide*,  $C_6H_5N\cdot HBr\cdot Br_2\cdot 2H_2O$ .—Pure pyridine was treated with an excess of dilute hydrochloric acid and then saturated with bromine. A bromine-colored oil is formed, which becomes solid upon exposure and loses its bro-

<sup>1</sup> This Journal, 19, 328.

<sup>2</sup> This Journal, 17, 859.

<sup>3</sup> This Journal, 19, 329.

mine odor upon warming. The crude product melts at 94° C., and that crystallized from alcohol at 118°-120° C. The crystals are orange-yellow. In sample I, the crude product was well washed with chloroform but not crystallized, II is the crude product, III is the crude product washed with chloroform and then crystallized from alcohol. I and II do not contain even a trace of chlorine. When dissolved in absolute alcohol and placed in a freezing mixture, the crystals form as prismatic bars very sharply defined.

|                     | Calculated for<br>$C_6H_5N.HBr.Br_2, 2H_2O.$ | Calculated for<br>$C_6H_5N.HBr.Br.$ | Found.           |
|---------------------|--|-------------------------------------|------------------|
|                     | I.   | II.                                 | III.             |
| Titrated bromine .. | 44.59  | 33.30                               | { 44.33<br>44.08 |
| Total " ..          | 67.36  | 66.61                               | { 66.55<br>66.51 |
|                     |  |                                     | 66.38<br>66.01   |
|                     |  |                                     | 67.96<br>....    |

*Pyridine Hydrobromide Perbromide*,  $C_6H_5N.HBr.Br$ .—Pure pyridine hydrochloride was dissolved in chloroform and brominated. Stellate masses of flat golden needles were obtained. These were dried and crystallized from alcohol. Free from chlorine. Melting-point 88° C.

|                        | Calculated for<br>$C_6H_5N.HBr.Br.$ | Found.           |
|------------------------|-------------------------------------|------------------|
| Titrated bromine ..... | 33.30                               | { 33.18<br>33.39 |
| Total " .....          | 66.61                               | { 66.66<br>66.82 |

*Pyridine Methyl Bromide Perbromide*,  $C_6H_5N.CH_2Br.Br$ .—Ostermayer<sup>1</sup> treats pyridine methyl chloride with bromine and obtains  $C_6H_5N.CH_2Br.Br$ , melting-point 48° C. Loses bromine in the air. Great difficulty was experienced in confirming Ostermayer's work. In one experiment a yellow compound was obtained free from chlorine, melting at 82°-83° C., which gave fairly good results for  $C_6H_5N.CH_2Br.Br$ .

|                        | Calculated for<br>$C_6H_5N.CH_2Br.Br.$ | Found. |
|------------------------|--|--------|
| Titrated bromine ..... | 31.46                                  | 32.09  |
| Total " .....          | 62.93                                  | 64.41  |

*Pyridine Methyl Bromide Dibromide*,  $C_6H_5N.CH_2Br_2$ .—Most of the experiments gave results indicating a compound between the dibromide and the tribromide. Finally, after several hours bromination, a product was obtained which crystallized from

<sup>1</sup> Ber. d. chem. Ges., 18, 599.

absolute alcohol in orange-colored needles and was entirely free from chlorine. Melting-point 55° C., not 48° C. as reported by Ostermayer. We brominated  $C_6H_5N.CH_2Br$  and get  $C_6H_5N.CH_2Br.Br_2$ . Melting-point 66° C.

|                             | Calculated for<br>$C_6H_5N.C_2H_5Br.Br_2$ . | Found.  |
|-----------------------------|---|---|
| Titrated bromine .....      | 47.87                                       | $\left\{ \begin{array}{l} 46.29 \\ 46.47 \end{array} \right.$ |
| Total        "        ..... | 71.80                                       | $\left\{ \begin{array}{l} 71.59 \\ 70.97 \end{array} \right.$ |

*Pyridine Ethyl Bromide Dibromide,  $C_6H_5N.C_2H_5Br.Br_2, 2H_2O$ .*

—Bromine vapors were passed through a water solution of pyridine ethyl chloride. A dark red oil was obtained which was warmed on the water-bath to remove excess of bromine. This oil would not solidify in a freezing mixture until a small piece of ice was added, when it became a mass of thin, reddish brown laminae, melting at 15° C., and solidifying at once when cooled below that temperature. This body was dissolved in absolute alcohol, using very gentle heat. It is decomposed by hot alcohol. Again, upon cooling, crystals could not be obtained until a small piece of ice was added, when it solidified as before. Melting-point 15° C. A qualitative test shows entire absence of chlorine.

|                             | Calculated for<br>$C_6H_5N.C_2H_5Br.Br_2, 2H_2O$ . | Found. |
|-----------------------------|--|--------|
| Titrated bromine .....      | 41.62  | 41.65  |
| Total        "        ..... | 62.44  | 62.61  |

**ACTION OF CHLORINE UPON CHLORIDES OF PYRIDINE.**

The effect of chlorine was studied upon the hydrochloride, methyl chloride, and ethyl chloride of pyridine in water solution. No perchloride is formed, for upon heating on the water-bath to remove the excess of chlorine the solutions do not liberate iodine from a potassium iodide solution.

*Molecular Weight Determinations.*—The cryoscopic method was used with a number of the above-described mixed perhalides, using phenol as a solvent. In most cases the results were not close but all plainly indicated the monopyridine molecule as the probable structure.

**SUMMARY.**

The range of formation with the periodides is great,  $C_6H_5N$ .

$\text{HI.I}$  to  $\text{C}_6\text{H}_5\text{N.HI.I.}$ , with the perbromides slight, and zero with the perchlorides. With the normal perhalides, increase in halogen lowers the melting-point. With the normal halide the hydrogen halide melts highest, the methyl halide lower, and the ethyl halide lowest.

In the mixed perhalides the power of displacement and the position of the halogen atoms in the molecule are points of great interest. Iodine in excess displaces bromine and chlorine completely, forming periodides from the normal bromides and chlorides. Bromine seems to displace iodine from the pyridine normal iodides and then combines with it to form a bromoiodide of a normal bromide. Bromine displaces chlorine completely, forming perbromides from the normal chlorides. Chlorine seems to displace both iodine and bromine at first to form normal chlorides, then it combines with the displaced halogen (some of the bromine always escapes) to form mixed perhalides,  $\text{ICl}$ ,  $\text{ICl}_2$ ,  $\text{BrCl}_2$ , of the normal chlorides, *e. g.*,  $\text{C}_6\text{H}_5\text{N.HCl.ICl}_2$ , from  $\text{C}_6\text{H}_5\text{N.HI}$  and  $\text{Cl}_2$ . The mixed perhalides containing bromine and iodine show color reaction for iodine when treated with carbon bisulphide, indicating that the iodine is probably present as periodine. Also the mixed perhalides containing bromine and chlorine show color tests for bromine, indicating that the bromine is perbromine. When an alcoholic solution of the perhalide containing bromine and iodine is titrated with sodium thiosulphate, evaporated to dryness, and the organic body thoroughly extracted; both bromine and iodine are found in the residue of sodium salts. In the following summary, unless references are given, the description of the preparations and needed references are found in the body of this paper:

1. *Action of Iodine upon Pyridine.*<sup>1</sup>

$\text{C}_6\text{H}_5\text{N.I}_4$ . Greenish black. Melting-point  $85^\circ \text{ C.}$

2. *Action of Bromine upon Pyridine.*

$\text{C}_6\text{H}_5\text{N.Br}_2$ . (?) Hofmann.

$(\text{C}_6\text{H}_5\text{N.Br}_2)_2\text{HBr}$ . (?) Grimaux.

$\text{C}_6\text{H}_5\text{N.Br}_4$ . Dark red. Melting-point  $58.5^\circ \text{ C.}$

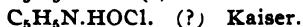
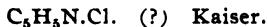
$\text{C}_6\text{H}_5\text{N.Br}_2$ . Light yellow. Melting-point  $94^\circ - 95^\circ \text{ C.}$

3. *Action of Chlorine upon Pyridine.*

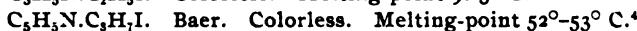
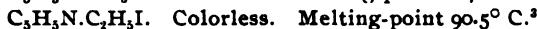
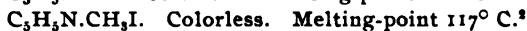
$\text{C}_6\text{H}_5\text{N.HCl}$ . Anderson.

$\text{C}_6\text{H}_5\text{Cl}_2\text{N.HCl}$ . Kaiser.

<sup>1</sup> This Journal, 17, 865.



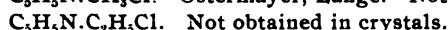
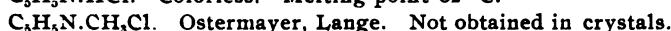
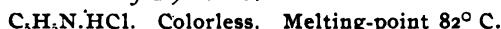
4. *Iodides of Pyridine.*



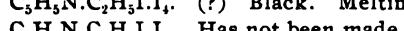
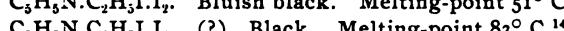
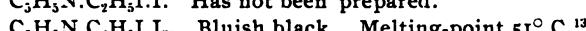
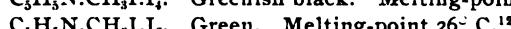
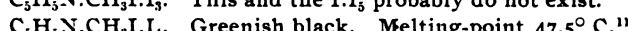
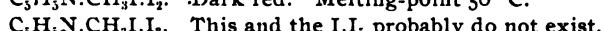
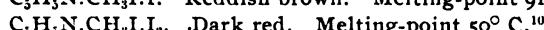
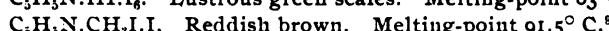
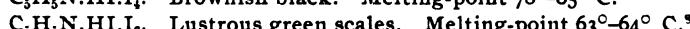
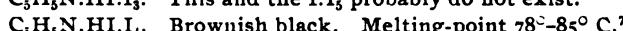
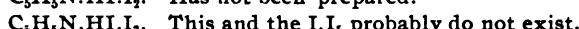
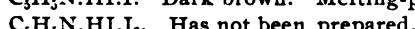
5. *Bromides of Pyridine.*



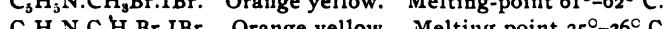
6. *Chlorides of Pyridine.*



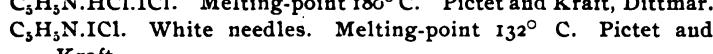
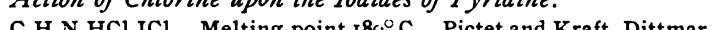
7. *Action of Iodine upon the Iodides of Pyridine.*



8. *Action of Bromine upon the Iodides of Pyridine.*



9. *Action of Chlorine upon the Iodides of Pyridine.*



<sup>1</sup> This Journal, 19, 327.

<sup>2</sup> This Journal, 18, 91.

<sup>3</sup> This Journal, 18, 92.

<sup>4</sup> This Journal, 18, 92.

<sup>5</sup> This Journal, 18, 93.

<sup>6</sup> This Journal, 19, 327.

<sup>7</sup> This Journal, 17, 867, and 19, 328.

<sup>8</sup> This Journal, 19, 328.

<sup>9</sup> This Journal, 17, 860.

<sup>10</sup> This Journal, 17, 860.

<sup>11</sup> This Journal, 19, 322.

<sup>12</sup> This Journal, 19, 323.

<sup>13</sup> This Journal, 19, 329.

<sup>14</sup> This Journal, 19, 32.



Dittmar.  
 $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{ICl}$ ,  $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{ICl}_4$ . Lemon yellow. Melting-point  $176^\circ \text{ C}$ .



Canary yellow. Melting-point  $185^\circ \text{ C}$ .



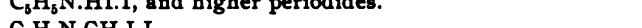
Yellow. Bally. Melting-point  $179^\circ$ – $180^\circ \text{ C}$ .



Bally. Melting-point  $90^\circ \text{ C}$ .

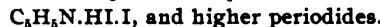


Ostermayer. Melting-point  $81^\circ$ – $82^\circ \text{ C}$ .

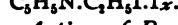


Canary yellow. Melting-point  $123^\circ \text{ C}$ .

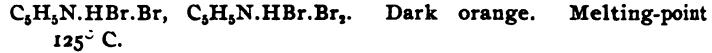
**10. Action of Iodine upon the Bromides of Pyridine.**



and higher periodides.



**11. Action of Bromine upon the Bromides of Pyridine.**



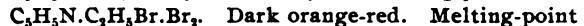
Dark orange. Melting-point  $125^\circ \text{ C}$ .



Light orange. Melting-point  $93^\circ \text{ C}$ .



Dark orange-red. Melting-point  $66^\circ \text{ C}$ .



Ostermayer. Melting-point  $48^\circ \text{ C}$ .



Dark orange-red. Melting-point  $35^\circ \text{ C}$ .

**12. Action of Chlorine upon the Bromides of Pyridine.**



Yellow. Melting-point  $19^\circ \text{ C}$ .



Red oil.

**13. Action of Iodine upon the Chlorides of Pyridine.**



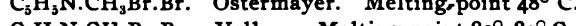
**14. Action of Bromine upon the Chlorides of Pyridine.**



Orange-yellow. Melting-point  $118^\circ$ – $120^\circ \text{ C}$ .



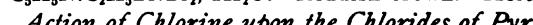
Golden yellow. Melting-point  $88^\circ \text{ C}$ .



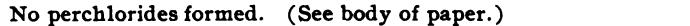
Ostermayer. Melting-point  $48^\circ \text{ C}$ .



Yellow. Melting-point  $82^\circ$ – $83^\circ \text{ C}$ .



Orange. Melting-point  $55^\circ \text{ C}$ .



Reddish brown. Melting-point  $15^\circ \text{ C}$ .

**15. Action of Chlorine upon the Chlorides of Pyridine.**

No perchlorides formed. (See body of paper.)

We wish to express our thanks to Professor A. B. Prescott, in whose laboratory and under whose general supervision the work has progressed. A paper on "Perhalides of Quinoline" is nearly ready, and work is continued upon "Halogen Derivatives of the Alkaloids with a View to Methods of Analysis."

## A MODIFICATION OF THE PERMANGANATE METHOD FOR THE DETERMINATION OF IRON.

By HAMILTON P. CADY AND ALFRED P. RUEDIGER.

Received April 30, 1897.

THE methods generally employed for the volumetric determination of iron, are the permanganate and Kessler's modification of the bichromate method. The general accuracy of these methods cannot be doubted and the only objection to them is the time that they consume. If potassium bichromate be used the titration may be made in the presence of hydrochloric acid, and stannous chloride can be employed as a reducing agent. The actual process of titration however is very tedious and in many cases is not as accurate as determinations by the permanganate method.

In using the old permanganate method, however, the solutions must be free from hydrochloric acid as potassium permanganate is decomposed by the acid in the presence of ferric salts. On this account the hydrochloric acid is usually driven off by evaporation with sulphuric acid, and the iron is afterwards reduced by zinc. This is at best a long and tedious process. If the hydrochloric acid is not driven off, the action of ferric salts must be prevented by the addition of some substance. The ferric salts seem to act catalytically,<sup>1</sup> for oxalic acid may be titrated in hydrochloric acid solution with potassium permanganate with perfect sharpness, and without a trace of chlorine being set free,<sup>2</sup> showing that the decomposition of the permanganate is not due to the hydrochloric acid alone.

The catalytic action of the ferric salts may be very much diminished by the addition of other salts such as the sulphates of magnesium, zinc, and manganese, and several methods have been devised in which advantage is taken of this property of these salts. The use of manganous sulphate for this purpose was first proposed by C. Zimmerman<sup>3</sup>. He gives a number of analyses showing the agreement between the results obtained from the hydrochloric and the sulphuric acid solutions. Zinc was used as the reducing agent.

Reinhart<sup>3</sup> improved Zimmerman's method by using stannous

<sup>1</sup> Ostwald's Foundations of Analytical Chemistry, p. 144.

<sup>2</sup> Ber. d. chem. Ges., 1881, 15, 779.

<sup>3</sup> Stahl und Eisen, 4, 704.

chloride as a reducing agent, removing any excess of the latter with mercuric chloride and adding sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid permits the formation of ferric phosphate, a solution of which is nearly colorless, and does not obscure the end-reaction as the yellow ferric chloride would otherwise do.

C. T. Mixer and H. W. DuBois<sup>1</sup> modified this method slightly and gave a number of analyses showing the close agreement between the results obtained by this and by other methods.

The electric conductivity of solutions of the mercuric halides shows that they are ionized to an extremely slight extent, while the mercuric salts of oxygen acids are dissociated normally.

Since compounds of slight ionization always result when their constituent ions meet, mercuric halides are invariably formed when a mercuric salt of an oxygen acid is added to a solution containing halogen ions. If an excess of the salts of the oxygen acid be added the presence of the mercury ions derived from its dissociation, will diminish the already very slight ionization of the mercuric halogen compound, until it is practically nothing. Hence the solution would contain no halogen ions. As is well known there must be dissociation or the formation of ions before a chemical reaction can take place, and under the conditions above mentioned there will be no formation of halogen ions, hence such a solution will show none of the characteristic reactions of the halogens.

As an illustration of the foregoing, it may be noted that silver nitrate will give no precipitate in a dilute solution of a chloride in the presence of an excess of mercuric sulphate, and also that silver chloride is moderately soluble in a solution of mercuric sulphate.

From these general principles we concluded that it ought to be possible to titrate iron with permanganate in the presence of hydrochloric acid if an excess of mercuric sulphate be added to the solution. A number of experiments to test this conclusion were then made, with very satisfactory results.

In order to compare the results obtained in hydrochloric and in sulphuric acid solutions the following experiments were tried:

<sup>1</sup> This Journal, 17, 405.

Five grams of ammonium ferrous sulphate dissolved in 500 cc. of water and 100 cc. of this solution were used for each titration.

|  | Per cent. of iron. |         |
|--|--------------------|---------|
|  | Found.             | Theory. |
| No. 1. Sulphuric acid alone.....   | 14.21              | 14.28   |
| No. 2. " " " .....   | 14.21              | 14.28   |
| No. 3. " " " .....   | 14.28              | 14.28   |
| No. 4. Sulphuric acid with 5 cc. hydrochloric acid, and mercuric sulphate..        | 14.21              | 14.28   |
| No. 5. Sulphuric acid with ten cc. of hydrochloric acid and mercuric sulphate..... | 14.28              | 14.28   |

In order to determine whether this process would be applicable where stannous chloride was used as a reducing agent, a number of tests were made upon ammonium ferric alum, and in these determinations and for all subsequent analyses the following solutions were employed.

*Solution A.*—A five per cent. solution of stannous chloride. This solution need not necessarily be freshly prepared, but a portion of it should give no precipitate when diluted with twenty times its volume of water and boiled. The solution may be kept in good condition by acidifying with hydrochloric acid and putting a few fragments of tin into the bottle.

*Solution B.*—Hydrochloric acid, of a specific gravity 1.10, made by mixing equal volumes of acid of specific gravity 1.20 and water.

*Solution C.*—A mercuric sulphate solution. This is made by adding to 200 grams of mercuric sulphate eighty cc. of sulphuric acid (conc.) and adding this paste to 800 cc. of water. (If a yellow precipitate of basic mercuric sulphate is formed add more sulphuric acid.) To this is added 100 grams of orthophosphoric acid, dissolved in a little water and the whole is diluted to one liter.

If a good quality of mercuric sulphate is not at hand the salt may be easily prepared by heating metallic mercury in a porcelain evaporating dish on a sand-bath, with one and a half times its weight of concentrated sulphuric acid, as long as fumes of sulphuric acid are given off or till a sample of the salt does not become moist on exposure to the air. The mercuric sulphate should be tested by dissolving a portion of it in water, acidulated with sulphuric acid, and adding hydrochloric acid. If a

precipitate is produced the salt must be reheated with sulphuric acid.

#### METHOD I.

A process of analysis that we have found to be convenient is to dissolve the substance in water with a varying quantity of hydrochloric acid and heat to boiling after diluting to 100 cc., reducing with stannous chloride, adding small portions at a time until the solution becomes colorless, and a droplet gives no coloration with potassium thiocyanate. In order to oxidize any excess of stannous chloride that may have been used, a solution of potassium permanganate is added drop by drop until a droplet of the iron solution gives a faint but distinct color with potassium thiocyanate; stannous chloride, not more than one or two drops, is then added very cautiously. This whole process should be carried on at a boiling heat. The solution is then cooled and fifty cc. of dilute sulphuric acid is added, and for every ten cc. of hydrochloric acid that has been used, add thirty-five cc. of the mercuric sulphate solution, dilute to 400 cc., and titrate with potassium permanganate as usual. If the process of reduction has been properly carried out there will be only a slight precipitate of mercurous chloride formed from the reducing action of the stannous chloride, but if any great excess of stannous chloride has been added a heavy white precipitate will result and in such cases the determination cannot be relied upon.

#### METHOD II.

The substance is dissolved, best in a small Erlenmeyer flask in fifteen cc. of hydrochloric acid (solution B), two cc. of mercuric sulphate (solution C) is added, the whole is heated to boiling, and stannous chloride is added in small quantities at a time. The precipitate that may be temporarily produced as each drop of the stannous chloride is added, will dissolve after boiling a few seconds, until all the iron is reduced, when the solution becomes colorless, and the addition of a single drop of stannous chloride produces a perceptible turbidity or a precipitate, which does not redissolve on boiling. This shows the end of the reduction. The contents of the flask is rinsed into a beaker and diluted to about 300 cc., fifty cc. of dilute sulphuric acid are added, and then forty-five cc. of the mercuric sulphate (solution

C). The solution is then ready for titration without cooling as the amount added should cool it sufficiently.

Method I can be used in all cases, while Method II (which is much shorter), can always be used where there is not too much insoluble residue, which might obscure the reaction at the end of the reduction.

#### ANALYSIS OF AMMONIUM FERRIC ALUM BY METHOD I.

|                           | Per cent. of iron<br>found. | Oxygen = 15.8.<br>theory. |
|---------------------------|-----------------------------|---------------------------|
| No. 1. ....               | 11.64                       | 11.62                     |
| No. 2. ....               | 11.66                       | ....                      |
| No. 3. ....               | 11.68                       | ....                      |
| No. 4. ....               | 11.61                       | ....                      |
| Average of 10 others..... | 11.67                       | ....                      |

#### ANALYSIS OF AMMONIUM FERRIC ALUM BY METHOD II.

|  |       |      |
|--|-------|------|
| No. 1. ....  | 11.74 | .... |
| No. 2. ....  | 11.74 | .... |
| By reduction with zinc in a sulphuric acid solution. |       |      |
| No. 1. ....  | 11.74 | .... |
| No. 2. ....  | 11.74 | .... |

The results obtained by Method II would naturally be higher than those by Method I on account of the removal of a little iron in the process of testing in the latter case.

#### APPLICATION OF THE PROCESS TO IRON ORES.

In the analysis of ores, if the material be soluble in hydrochloric acid, it is boiled for some time with ten to fifteen cc. of solution B, until completely decomposed. The addition of some of the stannous chloride solution to the hydrochloric acid hastens the process of decomposition. When the ore is completely decomposed, if Method I is to be followed, the solution is diluted to 100 cc. and reduced as described under the above head. If Method II is to be followed, which is usually the better, the solution is not diluted but the two cc. of mercuric sulphate is added at once and the process continued as described. If long boiling was required for the decomposition of the ore, the greater part of the hydrochloric acid may have been driven off. Under these conditions the precipitate formed by the addition of a small quantity of stannous chloride will not readily redissolve, even when considerable ferric salts remained in the solution. In

such a case a few more cubic centimeters of hydrochloric acid should be added. Ores not soluble in hydrochloric acid may be dissolved after fusion with potassium hydrogen sulphate and then reduced by either method.

## RESULTS.

| Name.                | Iron found.<br>Per cent. |
|----------------------|--------------------------|
| Limonite, No. 1..... | 35.08                    |
| " " .....            | 35.02                    |
| Limonite, No. 2..... | 54.37                    |
| " " .....            | 54.49                    |
| " " .....            | 54.49                    |
| Limonite, No. 3..... | 37.47                    |
| " " .....            | 37.43                    |
| Limonite, No. 4..... | 36.68                    |
| " " .....            | 36.68                    |
| " " .....            | 36.72                    |
| Maguetite, .....     | 71.87                    |
| " .....              | 71.64                    |
| " .....              | 71.64                    |
| " .....              | 71.87                    |

In the analysis of the magnetite the determination was made upon a small quantity of the ore, three-tenths gram in each case, so any slight error in reading the burette was increased. The analyses of the limonites Nos. 3 and 4 were made by two different persons independently, and in each case they were entirely unfamiliar with the process, and good results were obtained without practice. This shows these modifications are easily mastered, and not difficult of execution.

The solution of mercuric sulphate described above contained one gram of the salt in five cc., and since four grams of mercuric sulphate are required to completely non-ionize one gram of hydrochloric acid, it is evident that thirty-five cc. of the mercuric sulphate solution will not be sufficient for all the chlorine in ten cc. of hydrochloric acid (sp. gr. 1.10); but much of the hydrochloric acid will escape during the process of dissolving the ore, and experience has shown us that thirty-five cc. of the mercuric sulphate solution is sufficient to combine with the chlorine that is left.

If too little mercuric sulphate has been added, the solution will smell of chlorine after the addition of permanganate. On the other hand a very great excess of mercuric sulphate will lower

the ionization of the mercuric chloride until it becomes lower than that of the mercurous chloride (formed by the reducing action of stannous chloride), and then the latter will dissolve, forming mercuric chloride and mercurous sulphate. Since mercurous sulphate exerts a reducing action on permanganate, this will introduce an error into the determination. Our experiments have shown that anywhere from twenty-five to fifty cc. of mercuric sulphate solution to ten cc. of hydrochloric acid, will give accurate results in the presence of small quantities of mercurous chloride.

The points requiring special care in this process then are :

1. Use stannous chloride that is in good condition.
2. Have the smallest possible excess of stannous chloride present after the reduction is completed.
3. Carefully adjust the proportions between the mercuric sulphate and the hydrochloric acid.

The speed of this process leaves nothing to be desired. Less than three minutes, in the case of soluble salts, has been found sufficient time for solution, reduction, and titration.

In conclusion we wish to acknowledge our indebtedness to Prof. E. H. S. Bailey for his advice and many valuable suggestions during the progress of the work.

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#### A NEW APPARATUS FOR SULPHUR DETERMINATIONS IN IRON AND STEEL AND A USEFUL FORM OF WASH-BOTTLE.

BY RICHARD K. MEADE.

Received April 26, 1897.

THE writer has found the two forms of chemical apparatus mentioned below of much use in his work and describes them here, in the hope that they may prove of equal service to other analysts. The first description is that of an apparatus to be used in the determination of sulphur in iron and steel, by the method of conversion into hydrogen sulphide and absorption of the evolved gas, in an alkaline solution of lead nitrate.

The apparatus is shown, drawn to one-eighth scale, in Fig. 1. It consists of the following parts :

1. A half liter flask, of the "Joliet" pattern, such as is used in the laboratories of iron and steel companies. The flask is

fitted with a rubber stopper, having two holes, through one of which passes a funnel with glass stop-cock, and through the other a piece of glass tubing, bent at right angles about its middle point.

2. A one-ounce separatory funnel, cylindrical in shape, fitted with a two hole rubber stopper, provided with tubes for the admission and exit of the gases, as shown in the cut. The

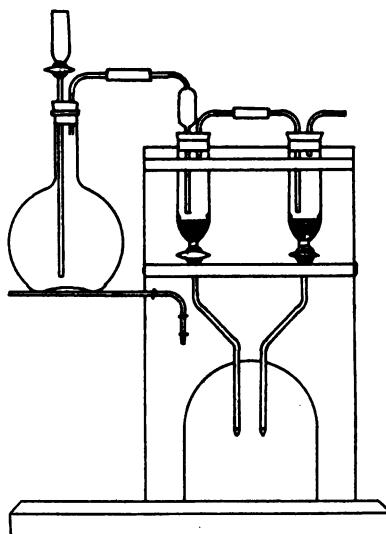


Fig. 1.

delivery tube is blown into a bulb of twenty-five to fifty cc. capacity, in order to prevent any of the solution in the funnel from being sucked into the evolution flask. The funnel itself is dented in three places, the same distance and about one-half inch from the bottom of the funnel, or just where the walls begin to narrow to meet the stop-cock. This may be easily done by cautiously heating the funnel in the flame of a blast-lamp and then pressing lightly at the desired points of indentation, with an iron wire. In the bottom of the funnel is placed a little glass wool, and upon this sufficient asbestos to reach even with the dents in the walls of the funnel. Over this a thin perforated disk of platinum, made to fit the funnel closely, is pressed down under the dents, holding the asbestos in place. The stems of the funnels are bent as shown in the sketch.

3. A separatory funnel, fitted similarly to the one described above, except that the tube leading into it need not be blown into a bulb.

4. A wooden base or stand upon which the whole rests. It is made exactly as shown in the sketch. The guide or upper cross piece is one and three-fourths inches wide and made solid. The rest, or lower one, is the same width, but is split along its middle, hinged at one end and fastened at the other by a catch, to allow the removal of the funnels when desirable. The iron ring, upon which the flask rests, is forged of one-fourth inch wrought iron and is fastened to the stand by means of staples.

The solution of the drillings, the preparation of the absorbent solution, and the precipitation of the sulphur as barium sulphate is conducted according to Blair, as described in his admirable book, "The Chemical Analysis of Iron."

The separatory funnels are half filled with an alkaline solution of lead nitrate, the sample weighed into the flask, the apparatus connected together and dilute acid poured upon the drillings. When action slackens, a lamp is placed under the flask and its contents boiled until all gas is given off. Pass a moderately rapid current of hydrogen through the apparatus for a few minutes and then disconnect the flask and funnels. Open the stop-cocks to the separatory funnels and allow the alkaline solution to run into a beaker, previously placed under them. The lead sulphide is caught by and retained upon the filters. Wash off the tubes into the funnels and pass a stream of water, from a wash-bottle, around the sides of the funnels several times, allowing the wash water to run through the filter into the beaker. Close the stop-cocks, remove the beaker under the funnels and put a clean one in its place. Drop a little powdered potassium chlorate, free from sulphur, into the funnels, and then add ten to twenty cc. of concentrated hydrochloric acid. Stand the apparatus in a hood, or where the fumes will be carried off readily, and open the stop-cocks of the funnels, allowing the acid to drop slowly into the beaker. As it passes through the filters it dissolves any sulphide which may be mixed with the asbestos. Wash the funnels and filters well with water, allowing the washings to run into the beaker. Heat the solution to boiling, nearly

neutralize with ammonia and precipitate the sulphur with barium chloride.

It very seldom happens that all the hydrogen sulphide is not absorbed by the solution in the first funnel, so that generally it is only necessary to collect and dissolve the precipitate formed in the first funnel; should any form, however, in the second funnel, this must be collected and dissolved, and the solution added to that from the first funnel. The solution in the second funnel may be used over for many analyses.

It is hardly necessary to caution chemists against allowing the solutions to stand for any great length of time, in the funnels, on account of their action upon the glass stop-cocks. The filters in the bottom of the funnels, if properly prepared, will last for many operations.

The apparatus may be used for the determination of sulphur by the method of absorption in cadmium chloride solution, with subsequent solution of the cadmium sulphide in hydrochloric acid and titration of the liberated hydrogen sulphide with iodine, or it may be used for determining sulphur by the Elliott method, or Drown's method of absorption in potassium permanganate solution. In either of the last two cases, the filters in the bottom of the funnels should be left out, since there is no need for them. The writer has found it much easier to wash out the funnels than  $\parallel$  tubes and potash bulbs, thus saving time and trouble and lessening the chance of error.

Many other uses will suggest themselves to the reader, to which the apparatus, modified in one way or another, may be put.

Fig. 2 represents a wash-bottle which the writer has had in constant use for some time and found very convenient. Its construction is so simple and evident from the drawing, that a description seems almost unnecessary. It consists of an ordinary wash-bottle, fitted up as usual, except that the shorter tube is made of heavy-walled glass tubing. To this is fastened a piece of hard wood, three-eighths by one-quarter by one and three-quarter inches, notched with a V-shaped notch across its face and, with a groove cut down its either side, parallel to the neck of the flask. A sketch showing the piece of wood, in detail, is appended to the drawing. A piece of stout wire is bent

with a loop at either end. The larger of these loops is made of sufficient size to admit the thumb comfortably and is covered

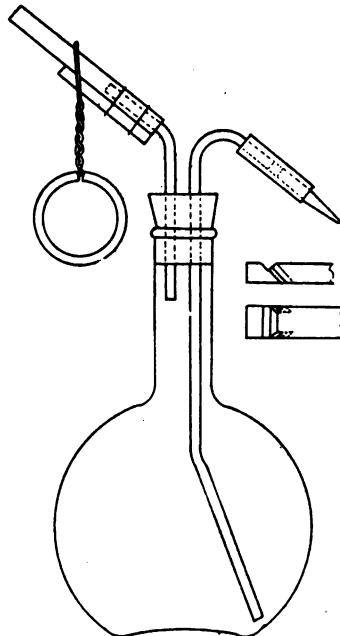


Fig. 2.

with a piece of small rubber tubing to prevent chafing that member. The smaller is bent over the rubber tubing and wood and is large enough to slide up and down freely in the vertical grooves, with about half an inch play. The bottle is grasped by the last three fingers of the hand and the thumb is passed through the loop in the wire, leaving the first finger free to guide the jet. A slight pull from the thumb is sufficient to bring the wire down upon the rubber, pressing the latter into the notch and effectually closing the opening. By doing this, before ceasing to blow into the bottle, the fumes of the acid, or steam, or whatever volatile substance the bottle may contain, are prevented from passing back into the mouth or lungs and a steady stream is kept going from the jet for some moments, or until the pressure of the thumb is relaxed, without further effort on the part of the operator.

## NOTES.

*A Simple Fat Extractor.*—To those making fat determinations in milk by means of solvents, the form of extractor represented in the accompanying cut will be found both convenient and accurate. It has been in use by myself and others for over three years, and in addition to being inexpensive and simple, it has been found capable of more rapid and fully as accurate work as many of the complicated and expensive forms of extractors. It consists of a small shallow dish spun out of very light copper, and fitted with two tight caps (see illustration). One is shallow while the other is longer, and perforated with several small holes on the bottom similar to a Gooch crucible. To use the extractor the shallow cap is fitted on the dish, as in the cut, then five cc. of milk are introduced and evaporated to dryness on a water-bath. I have found that one-half hour is usually sufficient to accomplish this, although, when porcelain milk dishes are used, three hours are considered necessary. The solids may now be weighed. The shallow cap is then removed, and placed inside the dish. The perforated cap having a thin layer of asbestos in the bottom, is put on, and the solids treated with the boiling solvent, ether or benzene. Care should be taken that the asbestos is so packed, that the solvent runs through slowly, say a drop every two or three seconds. The solution of the fat may be caught in a small beaker and the fat dried and weighed. I find that fifty cc. of the solvent is usually sufficient to remove all the fat, and although I have examined the residue many times for traces of fat, I have never succeeded in finding over one-tenth of one per cent. of the total fat present in the sample of milk. Were this dish made of platinum, instead of copper, besides being useful for various purposes in the laboratory, all the determinations called for in an ordinary milk analysis, for example, solids, fat and ash, could be made with a single sample, or five cc. of the milk under consideration.

VERNON J. HALL.

CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY,  
EVANSTON, ILL.



*The Exact Dilution of Liquid Reagents by Formula.*—While a full set of hydrometers should be included in the equipment of every general laboratory, there may be, nevertheless, occasions when such instruments are not readily available. But even where no such lack of apparatus exists, there are a great many cases when, I believe, it is far easier and more convenient to accurately prepare solutions of any required specific gravities by the use of a simple, general formula, rather than by hydrometer.

Quite frequently the dilution of a reagent is attended by a considerable rise of temperature, which must either be reduced before a hydrometer reading can be taken or else the latter must be corrected, an operation necessitating not only the use of a thermometer but also more or less calculation. Then, too, there are many occasions when the quantity of solution required does not afford sufficient volume to permit the use of an ordinary hydrometer.

Suppose it be required to prepare a volume,  $V_t$ , of a solution whose specific gravity shall be  $S_t$ , by the dilution of a volume,  $V_x$ , of a reagent whose specific gravity is  $S_x$ . The problem is to ascertain the volume,  $V_x$ .

$V_t - V_x$  = amount of water necessary for dilution.

From the equation  $V_x S_x + V_t - V_x = V_t S_t$ , it is found that  

$$V_x = \frac{V_t (S_t - 1)}{S_x - 1}.$$

Conversely, if it be required to dilute an exact volume of a liquid of certain specific gravity to one of different specific gravity, then by transposition :  $V_t = \frac{V_x (S_t - 1)}{S_x - 1}$ .

It is frequently required to dilute to a certain specific gravity with some reagent other than water. In this case, first consider water as the diluting agent, and find  $V_t$  as above. Then, if  $S_3$  = the specific gravity of the diluting reagent :  $\frac{V_t + V_x}{S_3} =$  the volume of the same necessary to be added to volume  $V_x$  to give a liquid of the specific gravity required.

CHAS. D. HOWARD.

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## OBITUARY.

MR. THEODORE A. HAVEMEYER, for many years a life associate member of the American Chemical Society, died at his home in New York City, on April 26. He was born in that city in 1839, and practically his whole life was devoted to the industry of sugar refining, in which he came to take such a prominent position in this country. The facts of his successful career, which will be of interest to the members of the Society, are so well set forth in an article in the *New York Sun* of April 26th, that we cannot do better than reproduce it.

"Theodore A. Havemeyer was of the third generation of the Havemeyers, noted for their great sugar industry in this country. He was the son of Frederick C. Havemeyer, whose father, Frederick Charles Havemeyer, with his brother, William S. Havemeyer, started a refinery in Vanderveer street, this city, in 1800.

"Frederick C., the father of Theodore A. and Henry O. Havemeyer, retired from the business in 1835, but in 1858 went into the business again for his sons, purchasing an interest in the Williamsburg Husse warehouse property.

"From that beginning grew the business that to-day practically controls the sugar industry of this country, and has a marked influence on that of the world. Every year the large brick factory between South Third and South Fourth streets was improved, and the four sons, associating in business with their brother-in-law, established the firm of Havemeyer & Elder.

"The firm took a lead in the sugar refining business from the start. They had fifty men in their employ at first, and the business increased until before the recent consolidation of many refineries throughout the country by them the factory there employed nearly 4,000 men.

"Of the four brothers who started in the business, Henry O. Havemeyer now alone remains. George Havemeyer was killed at the refinery in 1862, and Thomas Havemeyer afterward retired from the business.

"In speaking of the causes of his success in business some years ago, Theodore Havemeyer said :

"We were taught our business thoroughly. After leaving school I was sent to Europe to learn all I could concerning the business I was to follow for a livelihood. In 1857 I went to the Hamburg refineries, and thence, after quite a lengthy experience, I went to other cities of Germany, where I gained a knowledge of the most advanced methods of that day. On my return, in 1859, I went into my uncle's refinery in Vanderveer street, and from there I went into the business in Williamsburg. I made up my mind from the start that whatever was worth doing at all was

worth doing well. For twenty-five years I was at work at 7 A.M. and did not leave the refinery until 7 P.M. I never went to bed at night until I had gone through the whole establishment. Many times I worked all the night long. While I was a single man my expenses never exceeded \$50 a month. Pilot bread and cheese made for me many a meal. A canvas suit was my daily apparel, and there was no part of the business at which I and my brothers did not work ; no part we considered too dirty or too arduous or beneath us.

"One prerequisite in any business is a thorough mastery of its principles and a knowledge of all its details. There was no part of the manufactory or no part of the refining business with which we were not thoroughly familiar. I knew how to fire up under the boilers, how to run the engines. I built an engine once myself. I knew how to refine the sugar and how to market it. I knew what was a fair day's work for a man, because I worked alongside of the men. Another requisite is application and alertness. We were always on the lookout for some better way to do a thing, and our success is largely owing to invention brought out by observation and experiment. Another need is integrity and promptness in business dealings. We always paid cash as we went along, but if one has to give notes they should be promptly met. We filled our orders always according to agreement. Another rule is to keep away from liquor, and we always followed it. The practice of these rules, combined with frugality and ordinary facilities of mind, will bring commercial success to any man."

"The Havemeyers invented many labor-saving machines and methods, and by means of these and the immense capital employed, sugar, which was refined in their grandfather's time on a margin of 10 cents a pound, and in their father's time at 4 cents a pound, is to-day refined for 1 cent a pound.

"It was not alone in the sugar refining business that Theodore A. Havemeyer was prominent. His banking and real estate interests were enormous.

"Mr. Havemeyer was greatly interested in agriculture, and had one of the finest stock farms in the country at Rahway, N. J. Besides his handsome residence in this city, he had a magnificent summer home at Newport. He was interested in golf, and was really the father of golf in this country. He was President of the American Golf Association at the time of his death.

"For twenty-five years Mr. Havemeyer was the Austrian Consul-General in this city, having been appointed to succeed his father-in-law, Ritter von Loesy, in 1871. He resigned in 1895, and immediately there was much talk to the effect that he was to be ennobled by the Austrian Emperor.

"Mr. Havemeyer was 58 years old at the time of his death. He

was married 33 years ago to a daughter of Chevalier de Loesy, the then Austrian Consul-General here. He leaves a widow and nine children."

W.M. McMURTRIE.

### BOOKS RECEIVED.

**Variety Tests of Fruits. Tests of Vegetable Seeds.** Bulletin No. 44. March, 1897. 48 pp. Agricultural Experiment Station of the University of Illinois, Urbana, Ill.

**The Synchronograph. A New Method of Rapidly Transmitting Intelligence by the Alternating Current.** By Albert C. Crehore and George O. Squier. Reprinted from Vol. 14 of the Transactions of American Institute of Electrical Engineers, N. Y. City. 31 pp.

**Relations Between the Melting Points and the Latent Heats of Fusion of the Metals.** By Joseph W. Richards. 5 pp. Reprinted from the Journal of the Franklin Institute, May, 1897.

**Water and Public Health. The Relative Purity of Waters from Different Sources.** By James H. Fuertes. x+75 pp. New York: John Wiley & Sons. Price, \$1.50.

**A Page from the Chemistry of To-day.** By Charles A. Doremus, A.M., M.D., Ph.D. 23 pp. Press of J. J. O'Brien & Son, New York.

**The Story of the Chemical Elements.** By M. M. Pattison Muir, M. A. 189 pp. London: George Newnes, Ltd. Price, 50 Cents.

**The Book of the Dairy. A Manual of the Science and Practice of Dairy Work.** Translated from the German of W. Fleischmann, Ph. D., by C. M. Aikman and R. Patrick Wright. xxiv+344 pp. London: Blackie & Son; and New York: D. Van Nostrand Co. Price, \$4.00.

**Ninth Annual Report of the Storrs Agricultural Experiment Station, Storrs, Conn.** 1896. 292 pp. Report of the Director: Bacteria in the Dairy; Study of Rations Fed to Milch Cows in Connecticut; Investigations on Metabolism in the Human Organism—Preliminary Account of Experiments on the Income and Outgo of the body and the Effects of Different Diets; Studies in Dietaries; Various Digestion Experiments; Average Composition of American Food Materials; Field Experiments with Fertilizers; Analyses of Fodders and Feeding Stuffs.

**Proceedings of the Thirteenth Annual Convention of the Association of Official Agricultural Chemists held at Washington, D. C., November 6, 7, and 9, 1896.** Edited by Harvey W. Wiley, Secretary of the Association. Bulletin No. 49, U. S. Department of Agriculture, Division of Chemistry. 1897. 127 pp. Washington: Government Printing Office.

### ERRATA.

Page 390 (May number), line 9, for "bicarbonate" read "bi-chromate."

Page 414, Series 8, line 6, for "numbers" read "number."

Pages 420 and 421, at head of 3d column in tables, erase "Gms," (these numbers referring to cc. silver nitrate when amount of interferent is 0).

Page 427, Set III, second column, for "0.5" read "0.0."

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THE VALUE OF A BACTERIOLOGICAL EXAMINATION OF  
WATER FROM A SANITARY POINT OF VIEW.<sup>1</sup>

BY E. K. DUNHAM.

Received May 12, 1897.

SEVERAL years ago, when connected with the Massachusetts State Board of Health, the author had occasion to make bacteriological examinations of a large number of samples of water, derived from various sources. The method then in use was to mix one cc. of the water with about nine cc. of sterile nutrient gelatin, and to pour the mixture upon sterilized glass plates, where it solidified in a moderately thin layer. These plates were then kept under cover for two, three, or four days, to protect them from dust and from drying, after which they were examined either under the microscope, with a hand lens, or with the unaided eye. The number of colonies that developed on these plates was then recorded.

It appeared to me at that time, 1887, that it was not possible to judge of the quality of a water from the data so obtained. This opinion was supported in a striking manner by observations, of which the following is a good, though somewhat extreme, example. The water supply of one of the towns near Boston was derived from a series of driven wells, consisting of iron pipes forced into the sandy soil. All but one of these wells were connected with a pipe leading to the pump which drove the water into the town reservoir. The remaining well was not connected with the others, but was used for making observations

<sup>1</sup> Read at the Special Meeting of the New York Section, April 23, 1897.

on the level of the ground water. It was kept covered, except when used for that purpose.

I found that the water taken from the tap at the pumping station, after it had passed through the pump, contained two bacteria to the cubic centimeter, *i. e.*, it was practically sterile. Water taken from the observation well contained about 5,000 bacteria to the cubic centimeter.

The water in both cases was from the same source, namely the ground water, but that which passed through the closed pipes was protected from infection, while that from the observation well had been exposed to the entrance of bacteria from the air. The bacteria found in the water from this well were all of the same species, and the inference was plain that, of those bacteria which accidentally gained access to the water, only one species had found the conditions favorable for its indefinite multiplication. There could not be any doubt that the two waters were equally fit for drinking, provided the single species, which was present in such abundance, was unobjectionable. At that time the maximum number of bacteria that was considered permissible in a good water was set at 250; yet this perfectly wholesome water contained twenty times that number.

Similar observations soon led me to the conclusion that a water might contain a large variety of bacterial species without being injurious to health. The water of small brooks flowing from springs in wooded regions frequently contains numerous species of bacteria derived from the air and the banks of the stream, yet there is no reason to suppose that such water is unfit for drinking.

The manner, then in vogue, of interpreting the results of such a bacteriological examination by the plate method appeared to me to be artificial and inadequate, because the accepted standards of purity were based upon quantitative differences. The method itself was not wholly without value, for it appeared possible to gain some insight into the probable bacterial history of a water, by a simple inspection of the plate cultures, prepared from it. Pure waters, originally free from bacteria, but subsequently exposed to the atmosphere, when examined by plate culture, yielded colonies composed of bacteria, which, as a rule, failed to liquefy gelatin and frequently possessed chromogenic

powers. The water accumulating in collecting wells or trenches protected from surface drainage by walls of brick or stone and covered by structures permitting free ventilation, gave plate cultures of this character. The bacteria it contained were derived from the air.

Those waters which had received additions coming in contact with vegetation and the upper strata of the soil, contained the *bacillus subtilis*, the *bacillus mycoides*, and the *bacillus figurans*, all easily recognizable by the characters of the colonies resulting from their growth on gelatin plates. The waters of unpolluted brooks and small streams arising from springs in rural districts contained these bacteria, as well as those coming from the air.

It is doubtful whether any of the waters from larger streams or rivers, which I examined, were free from pollution by either sewage or waste from factories. The plate cultures from such waters revealed a varied flora, and it was not possible to identify, on the plate cultures, the species that I regarded as evidence of the presence of air bacteria and bacteria derived from the soil. It is probable that the bacteria resulting from the pollution of the water were more abundant or grew more rapidly than those from the air and soil and, in consequence, concealed their presence.

Plate cultures made from sewage and those prepared from waters that had certainly received sewage, contained colonies of a yellowish or brownish color, when viewed under the microscope. They were round, oval or lenticular in shape, and usually presented a multicontoured appearance, if the plates were not too crowded. These colonies I now believe to have been those of the common colon bacillus. The practically constant presence of such colonies, on plates from water contaminated with sewage, led me to look upon them as an indication of dangerous pollution.

I think there were good grounds for the opinion I then formed that the mere number and variety of bacteria in a water are of comparatively little significance, but that the presence of certain species might be accepted as indicating that the water had been exposed to certain pretty definite conditions before it was submitted to bacteriological examination, and that a knowledge

of those conditions was of importance to a just estimation of the probable risk of drinking the water.

The chief aim of an examination of water with reference to its fitness for drinking is to learn whether it contains, or is likely in the future to contain, poisonous substances, or the contagia of disease. The detection of mineral poisons falls within the domain of chemistry. The actual isolation of specific bacteria of disease can only be done by bacteriological methods. But in the vast majority of the cases in which an examination of water is required, mineral poisons are not present in notable quantities, nor are pathogenic bacteria so abundant as to be certainly detected by the methods now available. The object of an examination of the water in these cases is to estimate the degree of probability that in some future time the particular water in question may become the carrier of infection. This question practically resolves itself into the detection of pollution with sewage, which may at some time contain dejecta from cases of disease. The usual chemical examination aims at detecting such pollution, and a bacteriological examination may be directed towards the same end. By the former method, the soluble substances, which are abundant in sewage, are estimated. By the latter, the bacteria derived from the intestinal tract and those of putrefaction, which thrive in solutions rich in animal organic matter, are sought, and, if need be, isolated. When sewage is mixed with water, both these methods for its detection are applicable, but it appears to me that the bacteriological test is capable of being the more delicate and precise of the two methods.

An exhaustive bacteriological examination which undertook the isolation of every species present in a given water, and endeavored to trace the way in which each species gained access to the water, would require a much wider and more exact knowledge of the distribution of bacterial species than we at present possess. And even if that knowledge were available, such an examination would require a very protracted study of the water. It appears necessary, therefore, to resort to a few simple procedures which are likely to give the information strictly required for a just conception of the general bacterial

history of the water and to base the judgment of the sanitary value of the water upon the results so obtained.

I will give a brief outline of the methods that appear to me most likely to furnish useful knowledge respecting the wholesomeness of a water from a bacteriological standpoint, assuming that the main questions to be answered are: (1) whether the water has been polluted with sewage, and (2) in case there are many bacteria in the water, whence they were probably derived.

It so happens that most of the bacteria found in the air are strict aerobes, *i.e.*, are incapable of growth, save in the presence of oxygen. We may take advantage of this fact to gain a rough idea of the number of bacteria in the water which owe their presence to aerial contamination. My plan is to prepare four gelatin plates, with one cc. of water on each plate, and to allow two of them to develop in an ordinary moist chamber, the other two being kept in an atmosphere of hydrogen. When those which have been exposed to oxygen are ready for counting, all four plates are examined and the number of colonies estimated. I will give examples of the two sets of observations, illustrating the results obtained by this method.

*Experiment I.*—Distilled water taken from a demijohn which had been exposed to contamination from the air for at least two weeks, was examined in this way. At the end of two days the plates grown with access of air contained 1,395 colonies. Those grown in hydrogen showed no colonies at all. The latter were then placed in a moist chamber, where they were exposed to oxygen for two days. At the end of this time they contained 1,469 colonies, showing that the bacteria in the water were not killed by the hydrogen, but were incapable of growing to any great extent when in an atmosphere of that gas.

*Experiment II.*—A similar experiment was made with croton water. The plates grown in air contained 135 colonies. Those grown in hydrogen contained 30 colonies, but, after exposure to the air, the number increased to 128 colonies. It seems, therefore, that the croton water contains species that were at least facultative anaerobes, and probably some that were not originally derived from the air.

Those bacteria that are capable of producing specific diseases are nearly all facultative anaerobes, so that it is safe to infer

that the distilled water taken for the first experiment was fit for drinking.

It is probable, from their microscopical appearance, that some of the colonies on the hydrogen plates from the croton water, were those of the *proteus vulgaris*, one of the bacteria most frequently found in putrefying organic matter, of animal origin.

Although the bacteria, prevalent in the air, are usually dependent upon the presence of oxygen for their multiplication, it must not be assumed that all the strictly aerobic bacteria, found in a water, have been derived from the air. Many of those occurring in the soil are incapable of growing without a supply of free oxygen. This is shown by the following experiment.

*Experiment III.*—One gram of soil from near the surface of the ground was introduced into a liter of water which had been sterilized by prolonged boiling, and after vigorous shaking, plates were prepared as in the preceding experiments. The plates grown in air contained 38,771 colonies, those grown in hydrogen 534 colonies. The general appearance of the two sets of plates was very different. The air plates contained numerous colonies of mycoides, figurans, and the hay bacillus. The hydrogen plates contained only a slight growth of figurans, visible under the microscope. The hay bacillus and mycoides did not develop on the plates grown in hydrogen.

If we now turn our attention to the results obtained by this method, when sewage is examined, we shall find that the number of facultative bacteria is very much greater in proportion to the number of strict aerobes, than was the case in the experiments with water, contaminated with species from the air or soil.

*Experiment IV.*—Plates were prepared, each with one cc. of sewage from one of the main sewers of this city. After twenty-four hours the colonies were estimated with the aid of the microscope. The air plates contained an average of 51,516 colonies, the hydrogen plates 49,871, a difference of only 645 in over 50,000.

*Experiment V.*—One cc. of the same sewage was added to one liter of sterilized distilled water, and with one cc. each, the plates were prepared. Those grown in air contained 260 colonies, those grown in hydrogen 278. In this case the number of colo-

nies on the hydrogen plates was greater than the number on the air plates, a circumstance that need occasion no surprise when we reflect that the sewage contained little masses of suspended matter that would prevent a perfectly uniform mixture with water, and might, therefore, easily cause some of the samples, taken for bacteriological examination, to contain more bacteria than others.

*Experiment VI.*—The diluted sewage used for the last experiment was allowed to stand at the room temperature for three days and the examination was then repeated. The plates grown in air contained 18,187 colonies; those grown in hydrogen 17,197.

The last three experiments show that a large proportion of the bacteria in sewage are probably facultative anaerobes, and that a considerable dilution of the sewage does not prevent a rapid multiplication of the bacteria it contains. Such a dilution would improve the chemical character of the water, but leaves its bacteriological character unchanged.

A comparison of the results of the six experiments, detailed above, demonstrates that the method used is capable of throwing considerable light on the significance of the bacteria found in a sample of water.

It would not do, however, to leave the consideration of that method without pointing out a possible source of error in the deductions, drawn from the results of these experiments. It might be that there were two sets of bacteria on the plates, one consisting of strict aerobes, and the other of strict anaerobes, and that one or the other of these groups would develop on the plates, according to whether they were exposed to oxygen or not. I believe myself justified in excluding this possibility, on the ground that the characters of the colonies on the hydrogen plates were essentially the same as some of those on the plates grown in the air, both when examined under the microscope and with the unaided eye. The fact that the hydrogen plates, when subsequently exposed to oxygen, contained practically the same number of colonies as those which were originally grown in the presence of oxygen, also tends to exclude the source of error we are considering.

The simple procedure used in the above experiments would not alone suffice to reveal the presence of sewage. We must

gain a more definite idea of the characters of the bacteria in the water, where it is shown to contain facultative anaerobes before we are justified in concluding that they are an indication of sewage contamination.

All sewage that receives human feces contains the bacillus coli communis, or if it does not, has been subjected to germicidal agencies that would also kill pathogenic bacteria, derived from cases of disease. It is fair to assume that ordinary sewage would also contain the common bacteria of putrefaction. We must, therefore, direct our attention to the means of demonstrating the presence or absence of those species in the water under examination.

I am inclined to believe that the best way to accomplish this is the application of the putrefactive test based upon the method proposed by Schardinger in the *Centralblatt für Bacteriologie und Parasitenkunde*, 16, 833, 1894.

To about ninety cc. of the water, ten cc. of a ten per cent. pepton, five per cent. salt solution, previously sterilized, are added. The mixture is made in a sterile Erlenmeyer flask, provided with a cotton plug. A strip of paper, impregnated with lead carbonate, is suspended over the mixture and the flask is then placed in the incubator at 37° C. for twenty-four hours. Under these conditions of temperature and nutrition, the colon bacillus and the bacteria of putrefaction readily multiply, and the latter cause the production of hydrogen sulphide, which discolors the lead paper. A pure water will not cause a darkening of the paper, but as it is possible that a water which would not cause infection, either at the time or in the future, might contain putrefactive bacteria, this test alone should not be relied upon to decide whether a water is fit for drinking or not.

In order to detect the presence of the colon bacillus a loopful of the above mixture, after the twenty-four hours of incubation, may be used for the preparation of a series of plate cultures in various degrees of dilution. From these plates there is no difficulty in obtaining pure cultures of that bacillus, which may be used for further cultures made for the purpose of definitely identifying it, and, especially, of distinguishing it from the bacillus equi intestinalis, which appears to be the most common species present in the feces of horses.

This method takes considerable time, and if it be desired to simply prove the absence of the colon bacillus, there is a shorter method which can be employed. It consists in inoculating a series of fermentation tubes, containing nutrient bouillon, to which two per cent. of glucose has been added, with the water under examination, using one cc. of water for each fermentation tube. The tubes are then placed in the incubator. The colon bacillus has the power of causing fermentation with a production of gas when grown in sugar solutions. This gas collects in the upright limb of the fermentation tubes. If no gas is found in any of the tubes, it may be assumed that the colon bacillus was absent. But if gas is found it does not prove that the colon bacillus was present, for other bacteria are capable of decomposing sugar with a production of gas. It then becomes necessary to isolate the bacteria in the fermentation tube with a view to determining the presence of the colon bacillus, a matter of no difficulty.

The procedures which are now outlined constitute those which are thought most likely to throw light upon the sanitary value of a water. Let me next call attention to the results obtained by their employment in the examination of some samples of water.

*Experiment VII.*—The results obtained from croton water were as follows:

1. Plate cultures grown in air contained 135 colonies.
2. Plates grown in hydrogen contained thirty colonies.
3. The putrefactive test blackened lead paper within twenty-four hours, and emitted a foul, somewhat fecal odor. Plate cultures from the putrefaction flask revealed the presence of the colon bacillus and the bacillus proteus vulgaris.
4. The fermentation test showed a production of gas, and cultures made from the fermentation tubes revealed the colon bacillus.

It seems safe to infer from these results that the croton water had been exposed to pollution with sewage, but that the latter had been greatly diluted, and probably also exposed to contamination from the air and admixture with some surface drainage. The latter inferences are based upon the large proportion of

aerobic bacteria in the water, and of colonies of mycoides and subtilis on the plates developed in the air.

*Experiment VIII.*—A reservoir water from a town near New York yielded the following results:

1. Plates grown in air contained 2,090 colonies.
2. Plates grown in hydrogen contained 165 colonies.
3. The putrefactive test caused no blackening of the lead paper.
4. The fermentation test showed the production of gas, but cultures prepared from the fermentation tubes failed to reveal the presence of the colon bacillus. There were a few colonies of mycoides on the plates grown in air.

The evidence furnished by these results are in accord with the known facts about this water. They permit the inference that the water had not been contaminated with sewage, and was therefore free from putrefactive and intestinal bacteria, but that it had been exposed to the air and to contact with the upper layer of the soil.

If we accepted the simple enumeration of the bacteria in a water as a guide to a judgment of its purity, we should be erroneously led to consider croton water as purer than this reservoir water, whereas the methods actually employed show the reverse to be the case.

Where the presence of sewage and surface drainage is revealed by these methods, as in the case of the croton water mentioned, we should, in estimating the risk of infection from drinking the water, consider (1) the extent to which the sewage has been diluted, and (2) the dangers incident to the surface drainage.

That the dilution had been considerable is shown by the bacteriological examination, for the number of anaerobic bacteria was small, but the degree of dilution cannot be so accurately gauged by that method as by a chemical examination. Croton water, at the time this bacteriological examination was made, revealed nothing, on chemical examination, which would cause suspicion that it contained sewage. The dilution must, therefore, have been very considerable.

The danger from the surface drainage could only be estimated by a local inspection of the surroundings of the water.

The results of these examinations and the inferences drawn from them are in close agreement with the known facts regarding the croton and reservoir waters, and they tend to confirm the value of the procedures described.

But it does not always happen that the results of chemical and bacteriological examinations are in such close accord. I had occasion at one time to examine the water from a deep artesian well, and found the water practically free from bacteria. The chemical examination showed the presence of large quantities of the ammonias, nitrates, and chlorides, and the chemist's report strongly condemns the water. Local inspection revealed the fact that the fields around the well were used for the disposal of the sewage from a large penal institution in the neighborhood, and that the water from the well was used to supply that institution.

It appears to me, that under these conditions, which had persisted for years, the water might be considered as free from objections so long as the upper portions of the well remained water-tight. For it was evident that the percolation of the sewage through the soil removed the bacteria which it contained. The three modes of investigation reveal the conditions obtaining at the time and also point out the possible future dangers.

It would not do to regard the presence of the colon bacillus as a proof of pollution with sewage without other confirmative evidence. The feces of cattle and other animals contain that bacterium, and it is a pretty widely distributed saprophyte, especially in inhabited regions. The fact that it is found in milk, and, after a day or two, in the intestinal discharges of new-born children, is often cited as proof of its wide distribution. I do not think that too much stress should be given to that evidence when we consider the way in which children are born, and the way in which cows are usually milked. If the colon bacillus is present in a water in considerable quantities, as shown by a series of fermentation tubes, it is very unlikely that it gained access to the water in an innocent way.

When the colon bacillus reaches a water in company with sewage, there is sufficient organic matter of animal origin to furnish it with nourishment, favoring its rapid multiplication. We have had an example of this multiplication of the sewage

bacteria, of which the colon bacillus formed a considerable proportion in Experiment VI. In three days the number of bacteria rose from 260 to 18,187, an increase of nearly 600 per cent.

In order to gain a clearer idea of the conditions under which the colon bacillus would multiply in water, the following three experiments were instituted :

Three sterilized, cotton-plugged flasks each received one liter of distilled water, which was boiled in the flasks for one hour to sterilize it.

*Experiment IX.*—To one of these flasks one cc. of a filtered suspension of the colon bacillus, in sterilized distilled water, was added. The bacillus had been grown upon agar in order to get an abundant growth with the least admixture of organic matter from the nutrient medium. It was then carefully scraped off the surface of the agar and mixed with the sterilized water. After this the mixture was filtered in order to remove any considerable masses of bacilli not broken up during the mixing. After vigorous shaking the water in the flask contained 42,791 bacilli per cubic centimeter, as shown by plate culture.

The flask was kept at the room temperature, exposed to diffuse daylight. After twenty-four hours the water was again examined, when it was found that the number of bacilli had fallen to fourteen.

*Experiment X.*—The second flask received, in addition to the colon bacillus, one cc. of nutrient bouillon. After the mixture was made, the water in this flask contained 57,102 bacilli to the cubic centimeter. After twenty-four hours it contained 29,276.

*Experiment XI.*—The third flask received an addition of one cc. of an infusion of hay, instead of the bouillon. On the first day the water contained 14,030 bacilli. After twenty-four hours the number had fallen to 439.

These three experiments go to show that the colon bacillus, requires a considerable quantity of organic matter for its abundant multiplication. Dr. A. P. Hallock kindly made a chemical examination of the water in these three flasks, with the following results :

## PARTS IN 100,000.

|          |                          |         |
|----------|--------------------------|---------|
| Flask 1. | Free ammonia.....        | 0.00575 |
|          | Albuminoid ammonia ..... | 0.00175 |
| Flask 2. | Free ammonia.....        | 0.03675 |
|          | Albuminoid ammonia ..... | 0.2672  |
| Flask 3. | Free ammonia.....        | 0.0125  |
|          | Albuminoid ammonia ..... | 0.0008  |

Numerous experiments have been made by various investigators to learn the behavior of the colon bacillus when introduced into natural waters, both with and without previous sterilization. Their results have, in the main, been the same as those just given for these artificial mixtures. As a rule the number of bacilli decreased, but sometimes it remained about the same, or increased slightly, but not to the same degree as did the number of so-called "water bacteria" in the sample.

It seems to me that these observations support the belief that the colon bacilli, which accidentally gained entrance to a water, without an associated pollution with sewage, would fail to multiply to any great extent, and that they would certainly very rarely lead to erroneous inferences from the results of a bacteriological examination. Neither the colon bacillus nor the widely distributed proteus vulgaris cause the evolution of hydrogen sulphide when they are present in water submitted to the putrefactive test. So that an accidental presence of those bacteria would not be bacteriologically equivalent to admixture with sewage.

In this connection it would be of interest to know about the viability of the colon bacillus when subjected to desiccation and light.

The following experiments have a bearing upon this question:

Small threads of sterilized silk were moistened with bouillon cultures of the colon bacillus and then dried in a desiccator over sulphuric acid.

*Experiment XII.*—Bouillon culture grown in the incubator. Threads exposed to diffuse daylight. The bacillus failed to develop when the threads were placed in fresh bouillon after thirteen days of desiccation.

*Experiment XIII.*—Bouillon culture grown at the room temperature. Threads exposed to diffuse daylight. Bacillus dead after twenty days.

*Experiment XIV.*—Bouillon culture grown in incubator. Threads exposed to sunlight. Bacilli dead after six days.

*Experiment XV.*—Bouillon culture grown at the room temperature. Threads exposed to sunlight. Bacilli dead after ten days.

Similar experiments made with threads moistened with a suspension of human feces, gave the following results :

*Experiment XVI.*—When exposed to drying over sulphuric acid *in vacuo*, or under ordinary atmospheric pressure, and when exposed to diffuse daylight or direct sunlight, these threads all produced a distinct growth in bouillon after thirty-four days, when the observations were discontinued.

It therefore appears that the viability of the colon bacillus depends upon the conditions under which it is placed. There is apparently no danger of its speedy death when it is associated with fecal matter.

Experience shows that many natural waters, which might readily have received small quantities of the colon bacillus from dust or the surface of the ground, do not contain it in sufficient abundance for its detection by the methods described. This experience is in harmony with the results of the experiments here recorded.

It is, of course, conceivable that a good water might contain adventitious colon bacilli, and this possibility should be borne in mind when conclusions are drawn from the results of a bacteriological examination. It is not probable, however, that such a water would contain a large proportion of anaerobic bacteria, or give a positive outcome to the putrefactive test. If the colon bacillus appeared in considerable quantities in a water, as the result, for example, of drainage from barn-yards, it seems to me that it would indicate an objectionable pollution, even though it were no sign of the presence of human excreta. The author believes, therefore, that the possible conditions which might lead to erroneous inferences from the results of the bacteriological methods of water examination here described, do not seriously invalidate the conclusion that the plan offered is better calculated to give a just estimate of the fitness of a water for drinking purposes than the methods in more common use, and

that they are likely to be of considerable service in a sanitary examination of water.

It is hoped that those who are interested in the subject will put these methods to a practical test in order that their true value may be ascertained, through the experience resulting from their extensive employment.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. No. 29.]

## ON THE INFLUENCE OF VEGETABLE MOLD ON THE NITROGENOUS CONTENT OF OATS.

BY H. W. WILEY.

Received June 7, 1897.

In growing oats in pots containing vegetable soils from Florida, I noticed that the content of nitrogen in the product was much greater than in oats grown in common soils under the same cultural and climatic conditions. Previous to the beginning of the experiments described below I had noticed a peculiar condition of sugar-cane grown in Florida, on what is there known as muck soils. These soils are composed of vegetable mold, produced under the water in shallow lakes and along the banks of streams. A full description of these soils may be found in my paper on the "Muck Soils of Florida," published in Agricultural Science, 7, 106.

The condition referred to in the sugar-cane was manifested by a brownish color in the juice, which was extremely persistent, affecting even the color of the nearly pure sugar made therefrom. From the character of this coloration there is no doubt of its being due to an actual absorption by the growing sugar-cane of some of the components of the vegetable soil, or humus. The fact that plants, under certain conditions, have the faculty of absorbing humus has been subsequently confirmed by the experiments of Snyder.<sup>1</sup> The vegetable soils in which the oats were grown contain in the air-dried state over eighty per cent. of organic matter and less than ten per cent. of sand, and other mineral ingredients. The composition of four samples is shown in the following table:

<sup>1</sup> Bull. No. 41, Agricultural Experiment Station of Minnesota.

|  | Laboratory number. |           |           |           |
|--|--------------------|-----------|-----------|-----------|
|  | 13747              | 13748     | 13749     | 13750     |
| Per cent.                              | Per cent.          | Per cent. | Per cent. | Per cent. |
| Moisture .....                         | 10.30              | 11.52     | 8.84      | 9.35      |
| Organic matter and combined water .    | 83.30              | 82.21     | 82.77     | 83.72     |
| Total nitrogen .....                   | 2.54               | 2.59      | 2.76      | 2.68      |
| Albuminoid nitrogen .....              | 2.44               | 2.37      | 2.73      | 2.52      |
| Amid nitrogen .....                    | 0.10               | 0.22      | 0.03      | 0.16      |
| Nitrogen as nitrates and ammonia salts | 0.03752            | 0.07952   | 0.05600   | 0.08120   |
| Nitrogen as ammonia salts .....        | 0.03698            | 0.05600   | 0.03510   | 0.03360   |
| Nitrogen as nitrates.....              | 0.00054            | 0.02352   | 0.02090   | 0.04760   |

Sample No. 13,747 is a virgin soil from the best muck land on the Department Experiment Station near Narcoossee, Florida.

No. 13,748 is from the poorest virgin soil, sample No. 13,749 from a cultivated plot producing good sugar-cane, and No. 13,750 from a cultivated plot where cane failed to grow.

In the mineral constituents of the soil the following quantities of potash and phosphoric acid were found.

|   | 13747 | 13748 | 13749 | 13750 |
|---|-------|-------|-------|-------|
| Per cent. of moisture in air-dried material | 10.30 | 11.52 | 8.84  | 9.35  |
| Loss on ignition.....                       | 92.87 | 92.91 | 90.80 | 92.36 |
| Mineral matter <sup>1</sup> .....           | 7.13  | 7.09  | 9.20  | 7.64  |
| Potash <sup>1</sup> .....                   | 0.056 | 0.057 | 0.055 | 0.055 |
| Phosphorus pentoxide <sup>1</sup> .....     | 0.066 | 0.057 | 0.088 | 0.173 |

It is seen from the above data that the soils are deficient both in potash and phosphoric acid, containing generally only about 0.05 per cent of these ingredients except in one instance, where the percentage of phosphoric acid reached almost 0.2. While the data show the almost entire absence of potash, yet the cultures in pot experiments have demonstrated the fact that these soils respond more promptly to treatment with a phosphatic fertilizer than any other, and that they are capable of acting upon the finely ground mineral phosphates of Florida in a manner which makes them easily available to the growing crop.

The soil from the best muck land was found to be entirely free of nitrifying ferments, a culture seeded with it showing no nitrification after forty days. The practical absence of nitric acid in the air-dried sample is therefore not surprising. On the other hand, the molds which produce ammonia in an acid soil appeared to be fairly active. On these soils the oats obtained in 1895 and 1896 were grown. It seems probable from the data

<sup>1</sup> Per cent. on dry material.

obtained that the two samples from the best and poorest soils were interchanged before reaching the laboratory. The crop secured in 1894 was grown on other soils, obtained from the same fields and entirely like those described above in every particular.

The experiments made in 1894 were of a preliminary nature and had for their object a study of the conditions of growth of oats and other crops, with a view to more systematic experiments subsequently. The analytical data relating to the nitrogen in those crops, however, are of so much interest as to demand a rather detailed discussion.

The pots used in the 1894 experiments were made of clay, with perforated bottoms. They were painted with black asphalt paint within and with a white lead paint without. They were thirty cm. in diameter and thirty-seven cm. deep. The bottom of each pot was covered with broken stone and the well mixed vegetable soil placed over this until the pot was full.

**STATEMENT SHOWING THE AMOUNT AND KIND OF FERTILIZER ADDED TO EACH POT.**

| No. of pot. | Fertilizer used.   |
|-------------|--|
| 1           | None.  |
| 2           | 36 grams lime mixed with soil.   |
| 3           | 3.6 " $K_2SO_4$ mixed with upper 6 inches of soil.                                       |
| 4           | 5.4 " Florida phosphate mixed with upper 6" soil.  |
| 5           | 5.4 " " " " 6" "   |
| 6           | 5.4 " slag " " " 6" "  |
| 7           | 5.4 " superphosphate " " " 6" "  |
| 8           | 3.6 " $(NH_4)_2SO_4$ .   |
| 9           | 3.6 " $K_2SO_4$ , 3.6 grams $(NH_4)_2SO_4$ ; 5.4 grams Florida phosphate.                |
| 10          | 36 " lime; 5.4 grams Florida phosphate.  |
| 11          | 36 " " 3.6 grams $K_2SO_4$ .   |
| 12          | 5.4 " Florida phosphate; 3.6 grams $K_2SO_4$ .   |
| 13          | 5.4 " superphosphate; 3.6 grams $K_2SO_4$ .  |
| 14          | None.  |
| 15          | 36 " lime.   |
| 16          | 3.6 " $K_2SO_4$ .  |
| 17          | 5.4 " Florida phosphate.   |
| 18          | 5.4 " slag phosphate.  |
| 19          | 5.4 " superphosphate.  |
| 20          | 3.6 " $(NH_4)_2SO_4$ .   |
| 21          | 5.4 " slag phosphate; 3.6 grams $K_2SO_4$ .  |
| 22          | 36 " lime; 5.4 grams $NaNO_3$ .  |
| 23          | None.  |
| 24          | 36 " lime; 5.4 grams Florida phosphate; 3.6 grams $K_2SO_4$ ; 3.6 grams $(NH_4)_2SO_4$ . |
| 25          | 5.4 " $NaNO_3$ .   |
| 26          | 36 " lime; 3.6 grams $H_2SO_4$ ; 5.4 grams superphosphate.                               |

*Nitrogen in the Crop.*—The weight of the crop produced and the percentage of nitrogen in the roots, straw, and grain, respectively, are given below. In this connection attention should be called to the fact that, in some instances, a few of the grains were carried off by the sparrows in spite of the watchfulness of the attendant.

TABLE SHOWING WEIGHT OF CROP FROM EACH POT AND QUANTITY OF NITROGEN IN ROOTS, STRAW, AND GRAIN.

| Pot No.   | Weight of roots.<br>Grams. | Nitrogen in roots.<br>Per cent. | Weight of straw.<br>Grams. | Nitrogen in straw.<br>Per cent. | Weight of grains<br>in straw. and chaff.<br>Grams. | Weight of Nitrogen<br>in grains and straw.<br>Grams. | Average per<br>cent. nitrogen<br>in grains and straw.<br>Crop 1894.<br>Per cent. |
|-----------|----------------------------|---------------------------------|----------------------------|---------------------------------|--|--|--|
| 1         | 4.920                      | 1.82                            | 15.512                     | 2.05                            | 1.530  | 2.69   | 2.10   |
| 2         | 2.970                      | 1.62                            | 15.070                     | 2.02                            | 3.120  | 2.75   | 2.15   |
| 3         | 4.450                      | 1.79                            | 13.250                     | 2.13                            | 1.510  | 2.75   | 2.21   |
| 4         | 8.860                      | 1.34                            | 36.010                     | 1.29                            | 2.160  | 2.58   | 1.36   |
| 5         | 6.560                      | 1.29                            | 36.320                     | 1.34                            | 4.020  | 2.69   | 1.47   |
| 6         | 6.820                      | 1.29                            | 35.100                     | 1.12                            | 5.920  | 2.52   | 1.32   |
| 7         | 10.350                     | 1.23                            | 32.470                     | 1.26                            | 3.850  | 2.55   | 1.40   |
| 8         | 5.670                      | 1.74                            | 14.760                     | 2.26                            | 0.770  | 2.24   | 2.25   |
| 9         | 8.850                      | 1.68                            | 43.530                     | 1.85                            | 9.430  | 2.80   | 1.85   |
| 10        | 6.680                      | 1.79                            | 17.920                     | 2.29                            | 1.620  | 2.80   | 2.83   |
| 11        | 5.280                      | 1.82                            | 16.530                     | 2.18                            | 1.460  | 2.69   | 2.22   |
| 12        | 7.370                      | 1.23                            | 38.150                     | 1.15                            | 3.870  | 2.46   | 1.27   |
| 13        | 7.150                      | 1.06                            | 44.150                     | 1.11                            | 6.560  | 2.41   | 1.27   |
| 14        | 1.520                      | 1.57                            | 4.330                      | 2.24                            | 0.760  | 2.58   | 2.29   |
| 15        | 1.400                      | 1.79                            | 6.080                      | 2.69                            | 0.380  | 2.58   | 2.68   |
| 16        | 0.750                      | 1.68                            | 2.070                      | 2.21                            | 0.300  | 2.52   | 2.25   |
| 17        | 6.100                      | 1.18                            | 34.830                     | 1.40                            | 2.530  | 2.69   | 1.49   |
| 18        | 7.150                      | 1.46                            | 32.650                     | 1.47                            | 2.170  | 2.58   | 1.54   |
| 19        | 6.030                      | 1.34                            | 33.230                     | 1.75                            | 2.370  | 2.75   | 1.82   |
| 20        | 1.260                      | 1.90                            | 3.520                      | 2.63                            | 0.320  | 2.80   | 2.64   |
| 21        | 5.710                      | 1.12                            | 32.980                     | 1.46                            | 1.720  | 2.46   | 1.53   |
| 22        | 1.860                      | 1.79                            | 5.830                      | 2.63                            | 1.370  | 2.58   | 2.62   |
| 23        | 1.430                      | 1.68                            | 3.880                      | 2.52                            | 0.420  | 2.46   | 2.51   |
| 24        | 3.230                      | 1.85                            | 6.320                      | 2.69                            | 1.530  | 2.46   | 2.65   |
| 25        | 1.780                      | 1.85                            | 4.530                      | 2.69                            | 0.920  | 2.80   | 2.71   |
| 26        | 4.870                      | 1.74                            | 13.270                     | 2.69                            | 3.080  | 3.14   | 2.77   |
| Averages, |                            | 1.56                            |                            | 1.97                            |  | 2.63   | 2.02   |

The surprisingly high content of nitrogen in all parts of the crop is forcibly shown by the above data. In the unfertilized soils, where the weight of the crop was a minimum, the content of nitrogen is almost uniformly higher than in the fertilized samples, though of course the total weight of nitrogen entering the

crop is much less. The remarkable effect of phosphatic fertilizers in diminishing the percentage of nitrogen is strikingly shown in Nos. 4, 5, 6, 7, 12, 13, 17, 18, and 21. When the phosphate was applied in connection with nitrogenous fertilizers the reduction in the percentage of nitrogen was not so marked, as is shown by Nos. 9, 24, and 26. The data show that in these soils a phosphate is the only required fertilizer, and that it works equally well in each of the three forms in which it was used. In other words, these vegetable soils permit of the easy absorption of the finely ground phosphates without previous treatment with sulphuric acid.

The mean percentages of nitrogen in the three parts of the crop are very high, and this is especially the case in the straw and grain. In this connection it should be mentioned that the grains were ground and prepared for analysis without removing the chaff.

These results were so interesting that it was deemed advisable to repeat the experiments with fresh samples of the vegetable soil. Accordingly, in 1895, twelve pots were filled with vegetable soil, representing four different characters of soil, resembling, in their chemical analyses, the soils already mentioned. Since the roots of the oats crop are never harvested, it was deemed sufficient to confine the examination for nitrogen to the straw and grains. To facilitate the work the straw and grains were ground together so that one analysis was made to do for both. The fertilization of the pots is shown by the following tabular statement:

| No. of pot. |                         |
|-------------|-------------------------|
| 15          | Blank.                  |
| 17          | Phosphatic slag.        |
| 24          | Florida phosphate rock. |
| 26          | Blank.                  |
| 29          | Acid phosphate.         |
| 18          | " "                     |
| 23          | Blank.                  |
| 7           | Phosphatic slag.        |
| 28          | " "                     |
| 25          | Florida phosphate.      |
| 6           | " "                     |
| 16          | " "                     |
| 5           | Blank.                  |

The weights harvested from each pot, and the percentages of nitrogen in the straw and grains combined are shown in the following table :

| OATS.               |        |                           |                        |
|---------------------|--------|---------------------------|------------------------|
| Florida soil, 1895. |        |                           |                        |
| Pot No.             | No.    | Weight of crop.<br>Grams. | Nitrogen.<br>Per cent. |
| 15                  | 14,439 | 14.70                     | 1.82                   |
| 17                  | 14,440 | 56.70                     | 2.20                   |
| 24                  | 14,441 | 69.50                     | 1.53                   |
| 24                  | 14,442 | 37.20                     | 0.90                   |
| 26                  | 14,443 | 55.80                     | 1.01                   |
| 27                  | 14,444 | 47.20                     | 0.98                   |
| 29                  | 14,445 | 53.30                     | 0.95                   |
| 18                  | 14,449 | 52.03                     | 1.92                   |
| 23                  | 14,450 | 29.30                     | 1.03                   |
| 7                   | 14,451 | 51.41                     | 1.05                   |
| 28                  | 14,452 | 54.55                     | 0.72                   |
| 25                  | 14,461 | 40.71                     | 0.72                   |
| 6                   | 14,502 | 37.89                     | 0.92                   |
| 16                  | 14,503 | 52.99                     | 2.12                   |
| 5                   | 14,504 | 5.59                      | 1.37                   |

While the percentage of nitrogen is not nearly so high as in the results previously given, yet in many instances it is quite excessive. This is particularly so with Nos. 16 and 17, both of which had received phosphatic manures, the nitrogen in these samples being greater than in the unfertilized samples, in which the crop was almost a total failure. The effects of the phosphatic fertilizers, noticed in the first year's experiments, of diminishing the percentage of nitrogen, are not verified by the experiments made in 1895.

*Experiments made in 1896.*—Experiments made with the Florida vegetable soils were repeated in 1896 with a larger pot, made of metal, containing nearly twice as much soil as in the pots used in the previous years, but with no increase in superficial area. The soils in 1896 were not fertilized, but the character of the fertilizer carried over from the previous year is given in the subjoined table. The pots for 1896 being larger, were filled from two or more pots of the year previous, but the soil received no further fertilization. Any effect of fertilizer, therefore, which will be noticed in the crop is due to the continuous effect of the fertilizer from the previous year.

The character of the soil in each pot and the nature of the fertilizer residual from the amount added the previous year are shown in the following tabulation :

Pots 135, 136, 137, and 138 were filled with the Florida soil,  
No. 13,747.

Pots 139, 140, 141, and 142 contain soil No. 13,748.

Pot 143 contains soil No. 13,749.

Pots 144, 145, and 146 contain soil No. 13,750.

The residual fertilization of each of the pots is as follows :

| No. of pot. | Character of fertilizer.            |
|-------------|-------------------------------------|
| 135         | No fertilizer.                      |
| 136         | Florida phosphate.                  |
| 137         | Phosphatic slag.                    |
| 138         | Acid phosphate.                     |
| 139         | No fertilizer.                      |
| 140         | Florida phosphate.                  |
| 141         | Phosphatic slag.                    |
| 142         | Acid phosphate.                     |
| 143         | Florida phosphate.                  |
| 144         | No fertilizer.                      |
| 145         | Florida phosphate.                  |
| 146         | Phosphatic slag and acid phosphate. |

The weight of the crop harvested from each pot and the percentage of nitrogen in the straw and grain combined are given in the following table :

#### OATS.

Florida soil, 1896.

| Pot No. | No.    | Weight of crop.<br>Grams. | Nitrogen.<br>Per cent. |
|---------|--------|---------------------------|------------------------|
| 135     | 15,515 | 27.4                      | 1.71                   |
| 136     | 15,516 | 46.6                      | 1.53                   |
| 137     | 95,517 | 33.8                      | 1.09                   |
| 138     | 15,518 | 35.6                      | 1.23                   |
| 139     | 15,519 | 19.9                      | 1.98                   |
| 140     | 15,520 | 46.1                      | 1.81                   |
| 141     | 15,521 | 51.6                      | 1.75                   |
| 142     | 15,522 | 52.2                      | 1.79                   |
| 143     | 15,523 | 39.5                      | 1.11                   |
| 144     | 15,524 | 38.7                      | 1.01                   |
| 145     | 15,525 | 37.1                      | 0.97                   |
| 146     | 15,526 | 33.4                      | 1.06                   |

The above data show that the unfertilized soils had been

improved by two years of cultivation, so that they produced nearly as large a crop, at least in one instance, as those which had received fertilizers in the previous year. In two instances, *viz.*, pots 135 and 139, the unfertilized crop being small, showed the highest percentage of nitrogen, while in a third instance, *viz.*, 144, the percentage of nitrogen was quite low, but in this case the crop was quite large. In general, therefore, the data show that the addition of phosphatic fertilizers, as in the first year's experiments, tended to diminish the actual percentage of nitrogen in the crop harvested.

For the purpose of comparison, the nitrogen was determined in the straw and grains of oats grown in ordinary agricultural soils from six different states in 1895 and 1896. These samples were selected without reference to the content of nitrogen which they contained, but indiscriminately, for the purpose of securing samples of representative or typical soils. The average content of nitrogen in fourteen samples of straw and oats grown in 1895 in common agricultural soils from Missouri, Michigan, Illinois, Wisconsin, Maryland, and the District of Columbia was 1.13 per cent. These crops were grown at the experimental vegetation house of the Division of Chemistry under exactly the same conditions as attended the growing of the crops on the Florida soils, fourteen samples of which the same year showed an average content of 1.30 per cent. of nitrogen in the straw and grains. In 1896 the average content of nitrogen in twelve samples of oats grown on the representative agricultural soils from Missouri, Michigan, Illinois, Wisconsin, Maryland, and the District of Columbia was 1.04 per cent., while in twelve samples grown under identical conditions on the vegetable Florida soils the average content of nitrogen was 1.42 per cent. Thus, leaving out of the comparison altogether the data obtained from the analysis of the 1894 crop, it is seen that in the case of oats the content of nitrogen in the grain and straw is very much larger when the crop is grown on the vegetable mold than when it is grown on the ordinary agricultural soils from different parts of the country. When it is remembered that these vegetable soils are extremely rich in nitrogen, as was shown in the analyses given in the first instance, and when it is further considered that they are quite deficient in nitrifying ferments, it is fair to con-

clude that at least a portion of this excess of nitrogen which they contain is assimilated directly from the vegetable mold without previous oxidation to nitric acid.

*Relative Proportions of Proteid and Non-Proteid Nitrogen.*—The relative distribution of the nitrogen in the various samples between the proteid and non-proteid forms is also a subject of interest. In the crop of 1894 the average percentage of nitrogen in the whole crop was 2.02. The quantity of material at hand did not permit of the separation of the nitrogen in all the samples. This separation, however, was accomplished in thirty-one instances, *viz.*, in fourteen samples of the roots, eleven samples of the straw, and six samples of the oats and chaff. The average percentage of total and amid nitrogen in the classes named was as follows :

|                               | Roots.<br>Per cent. | Straw.<br>Per cent. | Oats and chaff.<br>Per cent. |
|-------------------------------|---------------------|---------------------|------------------------------|
| Total nitrogen (average)..... | 1.45                | 1.99                | 2.63                         |
| Amid    "     "     .....     | 0.32                | 0.70                | 0.35                         |

In the 1895 crop the separation was accomplished in fifteen samples of straw and grain together. The average percentage of total nitrogen in the samples examined was 1.27, and of amid nitrogen 0.44.

In the crop for 1895 the separation was accomplished in eleven instances, and the average percentage of total nitrogen found was 1.45, and the percentage of amid nitrogen was 0.29.

Comparing these relative percentages of amid and proteid nitrogen with crops grown in ordinary soils, it is found that in twelve samples grown in miscellaneous soils from different parts of the country in 1895 the percentage of total nitrogen was 1.15, and of amid nitrogen was 0.24, and in 1896, in fifteen instances of crops grown on miscellaneous agricultural soils from different parts of the country, the percentage of total nitrogen was 1.18, and of amid nitrogen 0.20.

It will be seen from the above data that the content of amid nitrogen in the crops grown in the vegetable soils was abnormally high, and that the content of proteid nitrogen in the crops grown on the vegetable soils was fairly comparable with the content of proteid nitrogen in the crops grown on miscellaneous soils. This is another important observation to be considered

in connection with the nitrogen content of the crop, and it is fair to infer from the data collected during the three seasons that the tendency of the vegetable soil rich in nitrogen is to increase the total nitrogen content of oats grown therein, but that this increase is chiefly due to the content of non-proteid nitrogen.

#### CONCLUSIONS.

(1.) Oats grown upon humus soils contain about twenty-five per cent. more nitrogen than those which are grown upon ordinary agricultural soils.

(2.) The increase in the amount of nitrogen noted above is found chiefly in the amid, and not in the proteid nitrogen.

(3.) Fertilization of humus soils, such as were used in these experiments with potash and nitrogenous fertilizers, did not have any appreciable effect upon the quantity of the crop.

(4.) The use of phosphatic fertilizers in connection with these humus soils greatly increases the quantity of the crop and diminishes the percentage of nitrogen contained therein. This diminution in the percentage of nitrogen appears to have resulted chiefly from the increase in the crop, and not to any deleterious influence of the phosphatic fertilizer.

(5.) The three forms of phosphatic fertilizer employed, *viz.*, finely ground soft Florida phosphate, phosphatic slag, and acid phosphate exert an almost identical influence in increasing the quantity of the crop.

(6.) Oats grown upon humus soils absorb directly therefrom a portion of the nitrogen contained therein, chiefly in the form of non-proteid nitrogen.

My thanks are due Mr. T. C. Trescot for his valuable assistance in the nitrogen determinations.

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#### NOTES ON THE DETERMINATION OF INSOLUBLE PHOSPHORUS IN IRON ORES.<sup>1</sup>

BY CHARLES T. MIXER AND HOWARD W. DUBOIS.

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ONLY within the past few years have chemists recognized the importance of the fact, that comparatively large amounts of phosphorus may occur in the siliceous residue left

<sup>1</sup> Read at the Chicago Meeting, 1897, of the A. I. M. E.

from the acid treatment of iron ores. We know of one case in which an ore contained about three times as much phosphorus in the insoluble as in the soluble form. It was disposed of at a premium, as an exceptionally high grade Bessemer ore containing 0.010 per cent. of soluble phosphorus, while the insoluble phosphorus brought the total amount up to 0.040 per cent.

The magnetite and the specular hematite of the Lake Superior districts, and the fine ores of the Mesabi range, as a rule, contain very small amounts of insoluble phosphorus. But the mining of the soft hematites and the progressive lowering of the phosphorus limit in a strictly Bessemer ore, have combined to make the determination of insoluble phosphorus one of the routine requirements in all analyses of Bessemer ores.

The insoluble phosphorus is understood to be that phosphorus which cannot be extracted by boiling hydrochloric acid of 1.10 specific gravity. The time given for the extraction of the soluble phosphorus will vary, of course, according to the nature of the ore. In ordinary practice the boiling is continued until the residue is white, or only very slightly tinged with ferric oxide. This ordinarily takes from half an hour to an hour. The prolonged boiling of ores known to contain considerable quantities of insoluble phosphorus has failed to extract any appreciable amount of additional phosphorus. Very fine grinding and subsequent sifting through bolting-cloth, has not increased the extraction. These statements represent the result of experiments carried out to test the opinions of a few chemists, who have maintained that such operations would materially increase the solubility of the phosphorus, generally supposed to be insoluble. The determination of this insoluble phosphorus in laboratories required to make a large number of analyses of ores daily, has added a considerable burden to the ordinary routine work.

The current practice in the treatment of the residue remaining from the acid solution of the ore, in order to transform the phosphorus into soluble form, is to fuse the siliceous residue with sodium carbonate in platinum crucibles, dissolve the fused mass in weak hydrochloric acid and evaporate to dryness to dehydrate the silica. The sodium phosphate is then extracted with weak hydrochloric acid and treated in the usual way for obtain-

ing the precipitate of ammonium phosphomolybdate. This operation requires considerable time and manipulation, and involves the introduction of sodium salts, which sometimes prove unfavorable to the obtaining of a pure precipitate of ammonium phosphomolybdate.

The practice of fusing the ore direct with sodium carbonate, and thus extracting the total phosphorus, requires larger platinum crucibles, and would not be practicable where so many determinations have to be carried on simultaneously, as in the case under consideration.

Hydrofluoric acid has been used to dissolve the insoluble residue, but care has to be taken to evaporate the excess of acid employed if the solution is to be subsequently placed in glass beakers.

Since there has been such increased demand for siliceous ores to mix with the low silica ores of the Mesabi range, chemists have been more than ever annoyed with the determination of insoluble phosphorus, as the increased amount of siliceous matter in the residue has required for fusion proportionately more sodium carbonate, heat, time, and patience.

For this reason we began a series of experiments with the purpose of finding a more rapid and convenient method of determining either the total phosphorus or the insoluble phosphorus by itself.

In the first experiment the ore was intimately mixed with less than an equal bulk of sodium carbonate, and then subjected to a red heat in a platinum crucible, the idea being to convert all the phosphorus into sodium phosphate, without using sufficient sodium carbonate to make a liquid fusion. The results were encouraging. The calcined mixture of ore and sodium carbonate are readily freed from the crucible and easily broken up by the pressure of a glass rod in the beaker. The mass was then boiled in some cases with water alone, and in other cases with weak acids, and the total phosphorus was quickly extracted from many ores containing considerable amounts of insoluble phosphorus. The main objection to this method was encountered, however, when the siliceous ores were treated by it. In such cases, owing to the large amount of siliceous residue, no matter how little sodium carbonate was used, it was difficult to prevent

a partial fusion, forming silicate of sodium, and thus making it hard to remove the calcined mass from the crucible.

Calcined magnesia was next tried as a base to combine with the insoluble phosphorus, and excellent results were obtained, no trouble being experienced with the fusion of the large silicious residues. It was, however, somewhat surprising that the magnesia acted so readily in extracting the phosphorus.

In the experiments next made the ore was calcined without the admixture of any base, and after this operation it was treated in the usual way with hydrochloric acid, when it was found that the total phosphorus had been extracted. This treatment was successful with most of the ores tried, but had the disadvantage of rendering the ferric oxide less readily soluble, and thus increasing the time required for the subsequent solution.

Applying this idea of simple ignition to the insoluble residues only, it was found that all the insoluble phosphorus could be thus converted into the soluble form, and a very simple practical method was thus established.

Very recently our attention has been called to the fact that Mr. Lychenheim<sup>1</sup> and Mr. Norris<sup>2</sup> had come to the same conclusion in the determination of phosphorus in coal and coke—namely, that fusion can be dispensed with and simple ignition substituted. Mr. Lychenheim has also informed the authors that he has found it to be perfectly satisfactory in the case of ores.

The details of our practice are as follows : About one and a half grams of ore are dissolved in a No. 3 beaker with twenty-five cc. of hydrochloric acid, 1.10 specific gravity. When the ore is dissolved, the excess of acid is evaporated until the solution begins to assume a syrupy consistency. It is then diluted with water and filtered into an Erlenmeyer flask, and the filter-paper and residue are placed in a platinum crucible and ignited. When the paper is burned off the residue is broken up with a platinum rod and ignited at a red heat for a couple of minutes, when it is removed and placed in a beaker for solution. Water is added, together with a few drops of hydrochloric or nitric acid, and the solution is brought to a gentle boil for about five minutes. It is then filtered into the flask containing the soluble

<sup>1</sup> A. I. M. R., 24, 66.

<sup>2</sup> *Ibid.*, 24, 862.

phosphorus (or into another flask, in case it is to be determined separately)<sup>1</sup>, neutralized with ammonia, and precipitated as ammonium phosphomolybdate. The latter precipitate is titrated according to Handy's modification of the sodium hydroxide method.

This method having been found by many tests to give perfectly reliable results, has been in use in our laboratory for more than a year. The following table exhibits a few of the many analyses made by us to satisfy ourselves as to the accuracy of the method.

In order to obtain some general idea of the nature of the base, which was combined with the phosphorus in the insoluble form, we made the following partial analysis of the insoluble residue from the hydrochloric acid treatment.

After drying the residue at 100° C., it was subjected to ignition in a platinum crucible for five minutes:

|                                      | Per cent. |
|--------------------------------------|-----------|
| Loss on ignition.....                | 5.05      |
| Loss due to extraction by acid*..... | 16.25     |

The residue from the above treatment contained, in percentages of the original residue:

|                                      | Per cent. |
|--------------------------------------|-----------|
| SiO <sub>2</sub> .....               | 74.25     |
| Al <sub>2</sub> O <sub>3</sub> ..... | 2.70      |
| CaO.....                             | 1.37      |

#### TABLE OF PHOSPHORUS DETERMINATIONS.

*Method A.*—Solution of ore and fusion of residue with sodium carbonate (old standard method).

*Method B.*—Solution of ore and ignition of residue without flux (proposed method).

*Method C.*—Ignition of ore without flux, and subsequent solution, determining total phosphorus.

<sup>1</sup> It has been found that it is better to determine separately the soluble and insoluble phosphorus. Otherwise a too dilute solution is liable to be obtained for the precipitation.

|     | Name of ore.          | Soluble phosphorus. | Insoluble phosphorus. | Total phosphorus. | Method. |
|-----|-----------------------|---------------------|-----------------------|-------------------|---------|
| 1.  | Winthrop <sup>1</sup> | 0.051               | 0.008                 | 0.059             | A.      |
|     | "                     | 0.051               | 0.008                 | 0.059             | B.      |
| 2.  | "                     | 0.039               | 0.008                 | 0.047             | A.      |
|     | "                     | 0.039               | 0.008                 | 0.047             | B.      |
| 3.  | "                     | 0.054               | 0.014                 | 0.068             | A.      |
|     | "                     | 0.052               | 0.015                 | 0.067             | B.      |
|     | "                     | ....                | ....                  | 0.067             | C.      |
| 4.  | "                     | 0.051               | 0.008                 | 0.059             | A.      |
|     | "                     | ....                | ....                  | 0.058             | C.      |
| 5.  | Cambria               | 0.052               | 0.004                 | 0.056             | A.      |
|     | "                     | 0.053               | 0.003                 | 0.056             | B.      |
| 6.  | Lillie                | 0.065               | 0.006                 | 0.071             | A.      |
|     | "                     | 0.065               | 0.007                 | 0.072             | B.      |
| 7.  | Lake Superior         | 0.021               | 0.006                 | 0.027             | A.      |
|     | "                     | 0.020               | 0.006                 | 0.026             | B.      |
| 8.  | "                     | 0.112               | 0.022                 | 0.134             | A.      |
|     | "                     | ....                | ....                  | 0.135             | C.      |
| 9.  | Salisbury             | 0.058               | 0.009                 | 0.067             | A.      |
|     | "                     | 0.058               | 0.010                 | 0.068             | B.      |
| 10. | "                     | 0.028               | 0.019                 | 0.047             | A.      |
|     | "                     | 0.028               | 0.019                 | 0.047             | B.      |
| 11. | "                     | 0.046               | 0.006                 | 0.052             | A.      |
|     | "                     | 0.046               | 0.016                 | 0.052             | B.      |
| 12. | Cleveland Hematite.   | 0.022               | 0.015                 | 0.037             | A.      |
|     | "                     | 0.022               | 0.016                 | 0.038             | B.      |
|     | "                     | 0.021               | 0.016                 | 0.037             | B.      |
|     | "                     | ....                | ....                  | 0.038             | C.      |

The solution (marked \*) from the ignited residue contained in percentages of the original residue :

|                                      | Per cent. |
|--------------------------------------|-----------|
| Al <sub>2</sub> O <sub>3</sub> ..... | 9.55      |
| CaO.....                             | 0.92      |
| B <sub>2</sub> O <sub>5</sub> .....  | 4.10      |

From the latter analysis it would appear that the greater part, if not all, of the phosphorus was combined with the alumina.

The conversion of the insoluble phosphorus into the soluble form by simple ignition is a matter of some theoretical interest. The formation of a more soluble phosphate under such conditions certainly does not appear probable. Possibly the method proposed by Berzelius<sup>2</sup> for the decomposition of phosphates, by means of silica and sodium carbonate, may involve a reaction somewhat similar to that which we have here under consideration.

<sup>1</sup> Nos. 1, 2, 3, and 4 are siliceous ores.

<sup>2</sup> Fresenius, 6th German edition, I, 416.

[CONTRIBUTION FROM THE LABORATORY OF BETHEL COLLEGE, RUSSELLVILLE, KY.]

## THE PHYSICAL EFFECTS OF VARIOUS SALTS AND FERTILIZER INGREDIENTS UPON A SOIL AS MODIFYING THE FACTORS WHICH CONTROL ITS SUPPLY OF MOISTURE.

BY J. L. BEESON.

Received June 4, 1897.

UPON making a comparative study of the physical properties of the Maryland soils, Milton Whitney has shown that the texture of the soil, or size of the soil particles, controls in the main the amount of moisture that each type of soil will maintain; and, therefore, determines the kind of crops best suited to each.

For early vegetables, where quick maturity rather than yield per acre is the desideratum, a large-grained, loose soil, containing from three to five per cent. of clay, which will maintain about six to eight per cent. of moisture, is best adapted. For a crop requiring a long period of growth, and when yield is an important item, the loose-grained soil will not do, but a fine-grained soil, containing a large percentage of clay, and which will maintain a high percentage of moisture, will be required. Upon this basis of the texture of the various types of soil in the state, the amounts of moisture which each will maintain, and the kinds of crops growing thereon, he has ascertained with considerable accuracy what crops are best adapted to each type of soil in the state. He has suggested that it is possible, by changing the potential on the surface of the soil grains, to pull together or push apart the clay and fine silt grains of a soil, and thus increase or decrease the size of the soil spaces, either by a rearrangement of the particles or by building up or breaking down the soil aggregates.<sup>1</sup> If this can be done, and at reasonable cost, it is clear that it would be of inestimable value to agriculture, for a farmer could thus change the texture of his soil, so as to adapt it to the best growth of that crop or crops which would bring the best price. If this is true, one naturally inquires what compounds will loosen the soil? What make it more compact, and in what degrees? He affirms, also, that "fertilizers have a very marked effect upon the texture of soils \* \* \* that we

<sup>1</sup> Bull. No. 21, Maryland Experiment Station.

have in our common fertilizers and manures very potent means of maintaining or changing the texture of soils, and thereby changing the conditions of moisture and heat which they can maintain for a crop, and that it is through this physical effect of manures and fertilizers in controlling the supply of moisture and heat within a soil under existing climatic conditions that the chief value of fertilizers and manures lies, rather than in the relatively small amount of plant food that they add to the soil."<sup>1</sup>

While this may be the case, Hilgard has pointed out the fact that it has not yet been proved, and claims that Dr. Whitney is maximizing the physical idea, and minimizing the plant-food conception of the use of fertilizers.<sup>2</sup>

Hilgard, in his researches upon the alkali soils of the arid regions and their reclamation, has shown that certain alkaline salts, and especially the neutral sodium carbonate when present in the soil even in very small quantities, so puddles the soil or breaks up the soil aggregates as to render the soil very retentive of moisture and exceedingly difficult to get into and to maintain even in tolerable tilth.

The conversion of the sodium carbonate into the sulphate by the use of gypsum, all but completely restores the soil to normal conditions, when a good crop may be grown. By this means large tracts of alkali lands have already been reclaimed. He also states that upon the edges of the alkali spots, when there is only a medium amount of alkali present, the crops are better than in lands in the same locality free from alkali, owing to the fact that the latter maintain more moisture.

These facts would, it seems to me, answer affirmatively Whitney's suggestion that it is possible so to alter the size or arrangement of the soil particles, in some cases at least, as to make the soil more retentive of moisture. But what salts effect the soil most? which ones build up and which break down the aggregates? and in what degrees? still remain to be answered. Also, do the ordinary fertilizer ingredients as added in the usual quantities in practice and which so handsomely increase the yield, affect appreciably the texture of the soil, and thus the soil's supply of moisture? These questions, it was believed, could quick-

<sup>1</sup> Bull. No. 21, Maryland Experiment Station, pp. 18-19.

<sup>2</sup> Agr. Sci., 6, Nos. 7 and 12.

est and best be answered by studying separately those factors which govern the supply of the soil's moisture in an untreated soil, and then in samples of the same soil to which various salts had been added and incorporated into the soil as in practice. Those factors which govern the storing and maintenance of a supply of soil moisture may be briefly stated as follows: (1) rate of saturation of the soil with water; (2) water-holding capacity; (3) after the soil is full of water, its conservation power (*a*) against the percolation of the water through the soil and therefore out of capillary reach, and (*b*) against the evaporation from the surface; and (4) finally the power of the soil to supply water to the root stratum by capillary action. Comparatively large quantities of various salts, when added to separate samples of a given soil, might be expected to modify appreciably the above-named factors of the soil. What would be the effect if the potassium of the soil were doubled as a chloride, sulphate, nitrate, carbonate, phosphate, etc.? if the lime were doubled as a sulphate, hydroxide, carbonate, etc.? if the magnesium salts? if the various commercial forms of nitrogen and phosphoric acid were doubled? What would be the effect if any *two* of these ingredients were added to the soil at the same time? if any *three* of them were added? What would be the effect of the various kinds of commercial fertilizers upon these factors? Should any of these salts have a marked effect in the quantities used, would it affect these factors appreciably, when added in the usual quantities in practice? While no attempt has been made to answer all of these questions in the work now reported, yet they serve to show the magnitude of the field and the importance of the line of inquiry. In order to deal effectively with the work it was necessary to devise a quick and accurate method of estimating these five factors which govern the soil's supply of moisture. Out of the necessities of the case grew the apparatus described below.

APPARATUS FOR THE ESTIMATION OF THE RATE OF ABSORPTION  
OF WATER BY SOILS, MAXIMUM AND MINIMUM WATER-HOLD-  
ING CAPACITY OF SOILS, RATE OF PERCOLATION OF  
WATER THROUGH SOILS, RATE OF EVAPORATION  
FROM SOILS, AND RATE OF CAPILLARY RISE OF  
WATER IN SOILS.

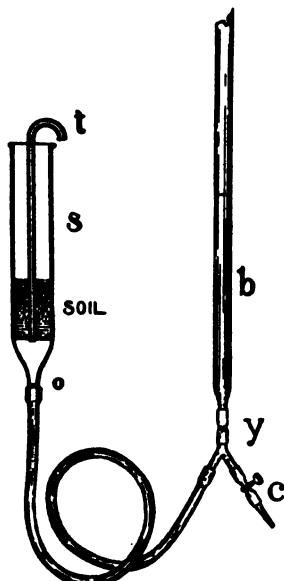


FIG. 1.

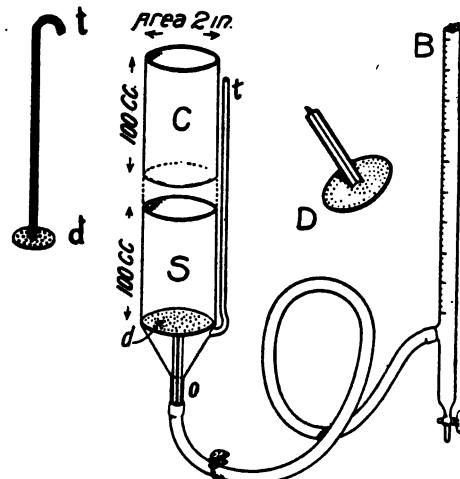


FIG. 2.

Fig. 1 shows the original form of the apparatus, the one with which the results embodied herein were obtained.

Fig. 2 shows the improved apparatus.

Apparatus 1 consists of a filter tube *S*, one and one-half inches in diameter, of such a height that it will hold 100 grams of ordinary soil. It is connected by means of a stout rubber tube to a 100 cc. side-tube burette, or by means of a Y-tube to an ordinary burette. A small glass tube is passed just through the center opening of a perforated copper disk, and fused in. The disk is of such a size that when a filter paper, perforated in the center, is slipped over the glass tube down upon the disk and the edges folded under, it will just fit the soil tube, *S*. The improved apparatus consists of a soil tube, *S*, of two square inches cross-

section, and which holds exactly 100 cc. Where the perforated disk,  $D$ , lodges there is a mark around  $S$ , so that the disk may be perfectly adjusted each time the instrument is used. The air tube  $t$  is on the outside of the soil tube, and enters it just below the perforated disk. The cylinder  $C$  is joined to  $S$  by means of a ground joint, and held in place by a wide rubber band. The improved form possesses the following advantages: (1) The soil tube may be stoppered and unstoppeder without settling or otherwise disturbing the soil; (2) the minimum water capacity can be readily determined with this instrument, but cannot be with the original one; (3) 100 cc. of the soil are weighed, and that weight taken each time when working with a given soil, and settled in the soil tube to the level. This insures an equal degree of settling in each case, a thing which is very essential in all work for comparative results. The instrument is now filled with water to the zero mark on the neck of the soil tube and on the burette. The pinch-cock at the end of the burette is of the greatest service in bringing the water to the zero mark. The zero mark may be gotten with the paper saturated or with it dry. In the latter case disks of a given size, in which the water capacity has been determined, should be used. The instrument is now ready for use.

*Rate of Capillary Rise.*—Add either 100 grams or 100 cc. of the soil to the tube  $S$ , settle by jolting a constant number of times, and raise the burette until the water is touching the bottom of the soil, where it is kept until the stratum of capillary moisture has reached the top of the soil. The time required for this is the rate of capillary rise for this height of soil column, and is obviously a function of size and shape of the capillary spaces.

. *Rate of Saturation.*—After the stratum of capillary moisture has reached the top, the burette is raised until its water-level is one-fourth of an inch above the top of the soil in the tube, where it is maintained. A stratum of maximum saturation, where the spaces in the soil are filled with water, slowly rises, and when it reaches the top and begins to form a surface of water on top of the soil the time is noted. The time required for the capillary ascent in this column of soil, plus that required for the maximum saturation, may be considered the rate of saturation. In

nature the rate of saturation is variable. In low places there will be a pressure from the head of water; on the high places no pressure. So the conditions of the experiment cannot be brought to reproduce those of nature. But for all comparative results the above method is accurate.

*Water-Holding Capacity.*—Experience has shown that in the case of very fine-grained soils some time is required for a complete saturation, so it is well to leave the water in contact with the soil, with the instrument stoppered, for an hour after the water has made its first appearance on the top of the soil, after which the burette is lowered and allowed to stand until the burette reading is constant. Then the burette is moved so that the water stands at the zero mark on the stem of the soil tube, where the number of cc. absorbed is read, which is also the percentage. Since the specific gravity of soils varies, and since it is desired to know the quantity of water a soil will hold to a given depth, it is better to ascertain these factors in terms of volume. The small tube  $t$  admits air below the disk as the burette is lowered, so that the water runs out of the soil by gravity alone, as in nature. Then it serves also to indicate the height of the water.

*Rate of Percolation.*—When the soil is saturated a head of one inch of water is so carefully added on top of the soil that the water is not muddied, and the time required for five cc. to run through is noted. In the improved instrument, a ground glass cylinder is attached, by means of a rubber band, to the top of the soil tube, to which the water is added.

*Rate of Evaporation.*—After removing the excess of water used in the preceding determination, from the top of the soil, expose the soil tube and contents to evaporation for any desired period of time. Saturate the soil again with water and read off the number of cc. absorbed, which is the amount of evaporation. Owing to the wide variation in temperature, hygrometric state, and motion of the air from hour to hour and from day to day, this method is of very little value for comparative results. But I would recommend it as a method of estimating the total evaporation during a season from a saturated soil, keeping the water in contact with the soil, and the burette and air tube stoppered.

*Minimum Water Capacity.*—This important factor in the study of the physical properties of the soil may be quickly determined by the use of the improved form of apparatus, as follows: When the soil tube is full and the soil saturated, attach cylinder C, and fill it gently with a portion of the same soil, air-dry. Allow it to absorb all the moisture it will, then remove and apply a new portion of the dry soil. Repeat until the dry soil will absorb no more moisture from the soil below. Cut off the soil even with the top of the soil tube S by means of a tight thread, then raise the burette and saturate the soil with water, noting the amount absorbed. The difference between this quantity and the maximum water capacity as previously determined, is the minimum water capacity of the soil. It is thus seen that all these six estimations may be rapidly and accurately made upon the same sample of soil, one after the other, without disturbing it in the apparatus.

#### THE CHARACTER OF THE SOIL EXPERIMENTED WITH.

The soil, obtained from the Louisiana Experiment Station at New Orleans, is dark alluvial deposit from the Mississippi river, and is quite retentive of moisture and exceedingly fertile. Below is given both the chemical and physical analysis of the soil:

#### CHEMICAL ANALYSIS.

|                               | Per cent. |
|-------------------------------|-----------|
| Insoluble matter.....         | 69.900    |
| Potash ( $K_2O$ ).....        | 0.687     |
| Soda ( $Na_2O$ ) .....        | 0.224     |
| Lime ( $CaO$ ) .....          | 0.882     |
| Magnesia ( $MgO$ ).....       | 1.288     |
| Iron oxide ( $Fe_2O_3$ )..... | 10.380    |
| Aluminá ( $Al_2O_3$ ).....    | 2.190     |
| Phosphoric anhydride .....    | 0.127     |
| Nitrogen .....                | 0.114     |
| Humus .....                   | 2.020     |
| S. G. { real .....            | 2.476     |
| apparent .....                | 1.170     |

#### PHYSICAL ANALYSIS.

|                               | Per cent. |
|-------------------------------|-----------|
| Fine gravel, 2-1 mm.....      | 0.10      |
| Coarse sand, 1-0.5.....       | 0.07      |
| Medium sand, 0.5-0.25 mm..... | 0.14      |
| Fine sand, 0.25-0.1 mm .....  | 0.58      |

|                                  | Per cent. |
|----------------------------------|-----------|
| Very fine sand, 0.1-0.05 mm..... | 14.40     |
| Silt, 0.05-0.01 mm .....         | 33.03     |
| Fine silt, 0.01-0.005 mm.....    | 10.70     |
| Clay, 0.005-0.0001 mm.....       | 31.99     |
| Total mineral matter .....       | 91.01     |
| Loss at 110° C .....             | 5.93      |
| Loss on ignition.....            | 3.91      |
| <br>Total.....                   | <br>99.85 |

The chemical analysis was made by one of my pupils, under my supervision, following the method adopted by the Official Chemists. The physical analysis was made by Mr. Matthews, under the supervision of Milton Whitney, Washington. The soil is neither the blackest and heaviest nor the lightest type of the Mississippi bottoms, and probably represents an average rich bottom soil. Several kilos of the soil were obtained dried, ground in a coffee mill, thoroughly air-dried, and then ground so that it would pass through a sieve of forty meshes to the inch. The sample contained about nine per cent. of moisture (8.786 per cent.) which probably represents the minimum moisture of the soil in a drought. The soil was thoroughly mixed, placed in bottles and sealed to prevent any change in moisture content. In the experiments described in this work all results are referred to 100 grams of this air-dried soil. The salts whose effects upon the physical properties of the soil it was proposed to study, were added directly, in a powdered form, to the soil and thoroughly incorporated with it, and the water used in the instrument was rain water, an effort being made to reproduce as near as possible the conditions in nature and in actual practice. The samples of soil, to which the various salts had been added, were kept in sealed bottles. The method of work was to study first the rate of absorption, water capacity, rate of evaporation, rate of percolation, and the capillary action of the untreated soil, then these factors in the samples, to each of which some salt had been added and incorporated. It is not claimed that the soil prepared in this way represents the exact conditions of a soil in nature, and therefore, that it will give the exact rate of saturation, percolation, etc., of a soil in the field. But it will show whether certain salts will so modify the above named factors as to change appreciably the soil's power of maintaining a

supply of moisture. The experiments described in the following pages were made with soil apparatus No. 1, with the soil tube one and one-half inches in diameter using fifty grams of the air-dried soil. No corrections were made for moisture, for this amount of moisture probably represents the soil's minimum moisture in nature.

### RATE OF SATURATION.

A study was made of the rate of absorption of water by the soil in each successive interval of time, as follows: Fifty grams of soil were placed in the soil tube and the burette raised so as to bring the water in contact with the soil. It was allowed to remain there for one minute, then the burette was lowered for one minute and the amount absorbed read off. This process was repeated each minute until the absorption became very slow, when the water was allowed to stay in contact with the soil for a longer period. Then the burette was lowered and left down until the reading was constant. Below is given the amount of absorption for each minute of contact:

|                                       | 7th       | 12th      | 17th      | 32d       | 47th      | 77th      |
|---------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Time of contact .....                 | to<br>1st | to<br>2nd | to<br>3rd | to<br>4th | to<br>5th | to<br>6th |
|                                       | m.        | m.        | m.        | m.        | m.        | m.        |
|                                       | Per cent. |
| Soil .....                            | 26.0      | 10.4      | 6.6       | 2.0       | 0.6       | 0.4       |
| " + 0.5 per cent. K <sub>2</sub> O    |           |           |           |           | 0.4       | 0.12      |
| as KCl.....                           | 16.2      | 4.0       | 2.0       | 2.0       | 1.0       | 1.1       |
| Soil + 0.5 per cent. K <sub>2</sub> O |           |           |           |           | 0.25      | 0.37      |
| as KNO <sub>3</sub> .....             | 17.8      | 5.6       | 2.8       | 2.2       | 1.4       | 1.2       |
|                                       |           |           |           |           | 0.36      | 0.3       |
|                                       |           |           |           |           | 0.2       | 0.17      |
|                                       |           |           |           |           | 0.18      | 0.17      |
|                                       |           |           |           |           | 0.15      | 0.15      |
|                                       |           |           |           |           | 0.05      | 0.05      |

A stratum of capillary moisture rapidly rose to the top and was slowly followed by one of saturation. These movements, as well as the rate of absorption, were greatly decreased by the presence of the potassium salts. In the cases of both the treated and the untreated soils the rate of absorption of the water during the first minute was very large and gradually decreased until near complete saturation, when it was very slow. In the case of the untreated soil nearly half of its water capacity, measured from air dryness, was satisfied the first minute of contact. The soil column was about two inches high, and no doubt the lower stratum of one-half to one inch in thickness was practically saturated the first minute. While the water is in contact with

<sup>1</sup> Absorbed 0.2 per cent. over night.

the surface of a soil (the lower surface in the apparatus) the films of water around the soil particles grow thicker and thicker, filling more and more nearly the capillary spaces. This gradually decreases the surface-tension and therefore the rate of absorption.

The rate of movement of the zone of capillary moisture is very much more rapid than the zone of saturation. This is due (1) to the decrease in surface-tension above mentioned, (2) to the resistance with which the water meets in passing through the saturated zone, (3) that the saturated zone holds several times as much moisture as the capillary zone, requiring a correspondingly longer time to saturate it. The resistance due to the passage of water through a saturated stratum must be considerable when it is remembered that the percolation per square inch, under a pressure of one inch on this soil, is one and four-tenths cc. per hour, while the rate of absorption was thirteen cc. the first minute. It will be noticed that the decrease in absorption the first minute in the cases when the salts were present is not proportional to that of the entire time required, for saturation, as compared against these rates in the untreated soil. This is doubtless due to the fact that the salts had not fully dissolved during the first minute of contact. Yet this change is soon noticeable as the time of contact increases, showing that the effect of the salts is extremely rapid. The whole time required for the saturation of the samples is the better criterion by which to judge the effects of the salts upon the soil, which are given below:

#### RATE OF COMPLETE SATURATION.

| Sample.  |  | Time.   |
|--|--|---------|
| Soil .....   |  | 35 min. |
| " + 0.5 per cent. K <sub>2</sub> O as K <sub>2</sub> SO <sub>4</sub> ..... |  | 60 "    |
| " + 0.5 " " K <sub>2</sub> O as KCl.....                                   |  | 180 "   |
| " + 0.5 " " K <sub>2</sub> O as KNO <sub>3</sub> .....                     |  | 180 "   |
| " + 0.5 " " K <sub>2</sub> O as K <sub>2</sub> PO <sub>4</sub> .....       |  | 130 "   |
| " + 0.5 " " K <sub>2</sub> O as K <sub>2</sub> CO <sub>3</sub> .....       |  | 35 "    |
| " + 0.5 " " K <sub>2</sub> O as KHCO <sub>3</sub> .....                    |  | 40 "    |
| " + 0.5 " " K <sub>2</sub> O as KOH .....                                  |  | 75 "    |
| " + 0.75 " " CaO .....   |  | 20 "    |
| " + 0.75 " " CaO as CaSO <sub>4</sub> .....                                |  | 30 "    |
| " + 0.75 " " CaO as Ca(NO <sub>3</sub> ) <sub>2</sub> .....                |  | 30 "    |
| " + 0.75 " " CaO as CaCl <sub>2</sub> .....                                |  | 25 "    |

| Sample.   | Time.    |
|---|----------|
| Soil + 0.75 per cent. CaO as $\text{CaH}_4(\text{PO}_4)_2$ .....    | 75 min.  |
| " + $\text{CaHPO}_4$ (0.75 per cent. CaO) .....                     | 70 "     |
| " + $\text{CaCO}_3$ (0.75 per cent. CaO) .....                      | 50 "     |
| " + 0.5 per cent. MgO as $\text{MgSO}_4$ .....                      | 90 "     |
| " + 0.5 " " $\text{Mg}(\text{NO}_3)_2$ .....                        | 60 "     |
| " + 0.5 " " $\text{MgCl}_2$ .....                                   | 60 "     |
| " + MgO .....   | 35 "     |
| " + 0.5 per cent. MgO as $\text{MgCO}_3$ .....                      | 35 "     |
| " + 0.5 " " $\text{Na}_2\text{O}$ as $\text{NaHCO}_3$ .....         | 36 hours |
| " + 0.5 " " $\text{Na}_2\text{O}$ as $\text{NaCl}$ .....            | 24 "     |
| " + 0.5 " " $\text{Na}_2\text{O}$ as $\text{Na}_2\text{SO}_4$ ..... | 80 min.  |
| " + 0.1 " " $\text{Na}_2\text{O}$ as $\text{NaHCO}_3$ .....         | 170 "    |
| " + 0.1 " " $\text{Na}_2\text{O}$ as $\text{NaCl}$ .....            | 5 hours  |
| " + 0.1 " " $\text{Na}_2\text{O}$ as $\text{Na}_2\text{CO}_3$ ..... | 105 min. |
| " + 0.1 " " N as $(\text{NH}_4)_2\text{SO}_4$ .....                 | 90 "     |
| " + 0.1 " " N as $\text{NH}_4\text{Cl}$ .....                       | 95 "     |
| " + 0.1 " " N as $\text{NH}_4\text{NO}_3$ .....                     | 120 "    |
| " + 0.1 " " N as $\text{NaNO}_3$ .....                              | 24 hours |
| " + 0.001 " " N as $\text{NaNO}_3$ .....                            | 45 min.  |
| " + 1 molecule CaO + 1 molecule $\text{NaNO}_3$ , .....             | 5 hours  |
| " + 3 " CaO + 1 " $\text{NaNO}_3$ , .....                           | 75 min.  |
| " + 9 " CaO + 1 " $\text{NaNO}_3$ , .....                           | 25 "     |
| " + 1 " $\text{Na}_2\text{SO}_4$ + 1 " $\text{CaSO}_4$ .....        | 60 "     |

It will be observed that almost every salt added to the soil has had some effect in changing the rate of absorption of water. The most of them have decreased it; in some cases enormously. The lime salts (save the phosphates and carbonate) alone increase it, and that to too a very small extent. The alkaline salts of potassium, ammonium, and sodium have affected it most, in the order named. It is rather singular that the carbonates of potassium should have no effect, and that the carbonates of soda should have such a marked effect. While the absorption of water by the soil during short heavy showers is an important factor in the water supply, the quantities of the fertilizer ingredients added in practice are not enough to affect appreciably this factor, except sodium nitrate, when added to the amount of 0.001 per cent. of nitrogen has reduced the rate of saturation about thirty per cent. It is further to be noticed that the addition of those salts which increase the rate of absorption, together with those which decrease it, have a neutralizing effect upon each other in the soil. Whitney has determined the surface-tension of various salt solutions and finds that certain salts

increase and others decrease the surface-tension of water. He attributes largely to this variation in surface-tension, the beneficial effects of fertilizers in modifying the soil's power to maintain a supply of moisture.<sup>1</sup> These variations in surface-tension, it seems to me, are too small to affect very appreciably the soil's supply of moisture. Then he finds that potassium chloride, ammonium sulphate, sodium nitrate, and sodium sulphate increase the surface-tension of water, and that potassium nitrate, ammonium nitrate, and potassium sulphate slightly decrease it. The former then should increase the rate of absorption of water by the soil, when present, and the latter should slightly decrease it. But the results given above show that all of these salts have decreased the rate of absorption, the size and arrangement of the soil particles remaining unchanged. It is clear then that the variations in rate of absorption due to the presence of certain salts, cannot be due to an alteration in the surface-tension. They are more likely due to the breaking-down of the aggregates of the soil into smaller ones, which would increase the ratio of the surface of the spaces to their volume, or to the rearrangement of the soil particles in such a way as to effect the same thing. If this be the cause, then these same salts ought also to decrease the rate of percolation and rate of evaporation, and increase the total capillary lift of a soil when present. Wolny has discussed the arrangement of the soil particles after the following manner: "If we consider a soil divided up into its individual particles, each particle sensibly spherical and of the same size, there are three simple arrangements of the particles, each giving a different amount of vacant space. First, when each sphere rests upon two spheres in the space between them, as in Fig. 3-A, giving a spherical-sided tetrahedron between them, having a cross-section A'; second, when each sphere rests upon a single sphere over its center, as in B, leaving a spherical-sided cubic space between, having a cross-section B'; and third, an arrangement the same as the first, except having every second particle in the alternate rows omitted, as in C, leav-

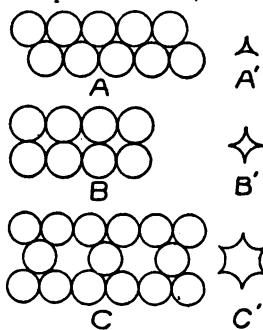


FIG. 3.

<sup>1</sup> Wiley's Agricultural Analysis, pp. 136-137.

ing a space with cross-section *C*. I would call attention to the fact<sup>1</sup> that aggregate particles of the soil as well as simple particles, are susceptible of these three arrangements, and they are more likely to be somewhat spherical than the individual grains. The total vacant space in the first arrangement would be 30.19 per cent. of the apparent volume of the soil, in the second arrangement 47.64 per cent., and in the third 48.7 per cent. In a rearrangement of the soil particles passing from the first to the second, or to the third, there would be quite a difference in the water capacity of the soil in each. Arrangement *C* has large and small spaces. The canals in the first arrangement are zigzag, in the other two they are straight, but with undulating sides. These facts alone would modify the rate of all kinds of capillary movements of water in the soil. If arrangements *A* and *B* be in combination, then the spaces will be over each other, as in arrangements *B* and *C*, giving a total space of 38.10 per cent. of the apparent volume of soil. In these three differently shaped canals there will be a difference in the ratio of volume of the spaces to the surface area bounding the spaces in each arrangement, and therefore different capillary values for water capacity, height of lift and capillary movements in each. While it is a fact that the soil particles are not spherical, but are more or less angular, the difference in the volume of space in these arrangements would be much greater than if the particles were spherical, and, therefore, the change in capillary values would be all the greater in passing from one form of arrangement to another. In arrangement *A* the water capacity and capillary movements would be least and the capillary lift greatest, for a given size soil particle. This change in arrangement can be brought about in nature and practice mainly by mechanical agencies, and is by no means under perfect control. Cultivation and heavy freezes tend to move the soil particles apart and to place them in the more open arrangement, while heavy rains and stirring or tramping when wet tend to break up the soil aggregates into finer ones and to place them in the compact form of arrangement. In a soil, however, the particles are not round, which would increase the variation in passing from one form of arrangement to another; and

<sup>1</sup> Experiment Station Record, 6, No. 9, pp. 744-5.

the particles are of variable sizes, and the smaller would tend to fill in the spaces between the larger. The two effects would tend to counteract each other, and to what extent would depend upon the ratio of the number of small to large particles. But in either of these three theoretical forms of arrangement, or in any other form of arrangement conceivable, the size of the soil particles, whether simple or aggregate, would determine the ratio of volume of spaces to surface area bounding them, and in a great measure all of the capillary values of the soil. Therefore, any agent which will change the size of the soil aggregates—which will build up larger ones, or break down those existing into smaller ones—will change profoundly that soil's power to hold and maintain a supply of moisture. While it is possible to control to a useful extent the texture of the upper layer of soil by judicious cultivation, so as to keep the crop mulched with a loose layer of earth, I think the results which are to follow will show that the size of the soil aggregates in the root stratum and sub-soil in the case of fine-grained soils, is also subject to control to a useful extent, and therefore the soil's power of maintaining a supply of moisture.

#### WATER-HOLDING CAPACITY.

The maximum water-holding capacity of any soil depends upon the total amount of space, and the size and shape of the individual spaces in the soil, and therefore upon the size and arrangement of the soil particles. In each of the three forms of arrangement of the soil particle of uniform size, there is a size of space which will just hold all its water and which represents the largest possible "maximum water-holding capacity" of that soil. If the size of the soil particle be increased or the arrangement changed so as to give larger spaces, these spaces will cease to be capillary and the water-holding power will be decreased, and if the spaces should be made smaller from any cause the water capacity of the soil would also be decreased. But in a natural soil the particles vary enormously in size. The spaces also vary in size, but very much less than the soil particles, owing to the tendency of the smaller particles to fill in the spaces between the larger ones. Yet in a natural soil, containing canals of various sizes, a certain porosity represents the

largest water capacity of that soil, when, if its grains be pulled further apart, some of the spaces will cease to hold water, and if pulled closer together the total space is made less, and in each case the water capacity is lessened. This is true not only for the maximum water capacity, but also for the water capacity at any point along the soil column in contact with water below—from the stratum below where all the capillary spaces are filled with water, to the top of the column where the water capacity is minimum, where only the finest capillary canals can sustain that height of column of water. Since the soil canals are of varying sizes, and each will sustain a different height of column, it follows that there will be a gradual decrease in the water-holding power from the bottom where it is maximum, to the top where it is minimum. Whether or not this decrease is regular will depend, in a soil chemically homogeneous, upon (1) whether or not the soil column is uniformly compact, (2) whether the arrangement of the soil grains is the same at all points along the soil column, and (3) whether or not the decrease in the size of the capillary canals is regular. These conditions we should not expect to realize in nature, and should therefore expect to find an irregular decrease in water capacity upon ascending such a soil column. The larger the number of small soil particles which can fill in the spaces between the larger ones, the less the variation in the size of the capillary canals, and, therefore, the less the difference between the maximum and minimum water capacities of the soil. Thus any agent which would decrease the size of the soil aggregates would tend to increase the minimum water capacity of the soil, which would be an important factor in plant growth during a dry season. It is to be regretted that the many other duties required of me have prevented me from making a full study of the effects of various salts upon the minimum water capacity of soils, which I hope to be able to do some time in the near future. The maximum water capacity in the soil alone and in the presence of the various salts experimented with was determined, but there was so little difference between that of the soil alone (which was 54.4 per cent.) and that of the samples to which the various salts were added, and the variations were so irregular that it is deemed not worth while to give their results here. None of the salts increased the

water capacity, and none decreased it more than six per cent. While the water capacity of the soil is an important factor in plant growth, since it represents the soil's supply of moisture, yet the variations due to the presence of the salts are too small to be of any practical value.

#### PERCOLATION OF WATER THROUGH SOILS.

During the absorption of rain by a soil the capillary action and gravity act together to move the water downward until the soil spaces are filled, when the surface-tension is zero and gravity acts alone to move the water downward. The water from the surface and from the spaces in the soil, which are too large to hold their water, thus tends to percolate through the soil. This movement of the water by gravity is resisted by the friction on the sides of the capillary canals of the soil, and whether due to the friction between water and water, or between water and the soil grain, or to both, the amount of resistance is proportional to the surface area bounding the spaces. It is clear then that the arrangement of the soil grains, whether simple or aggregate, according to one or more of the three possible ways, and also the size of the soil grains in any form of arrangement whatever, will affect this ratio of volume to area of bounding surface of the capillary canals. The size of the soil particles remaining the same, the arrangement in Fig. 3, A, would give the lowest rate of percolation and C the greatest. In any arrangement, the smaller the size of the soil particles or aggregate, the less the rate of percolation, and vice versa. A study was made of the percolation through the soil alone and in the presence of a few salts, as follows : Fifty grams of soil were placed in the soil tube (of one and one-half inches in diameter) saturated with water, and a head of one inch of water added on top of the soil, so gently that the water was not muddied, and the time required for five cc. to pass through was noted. The next day one inch head of water was added again and the rate of percolation noted, and so on until the rate became nearly constant, giving the results tabulated below :

## PERCOLATION PER HOUR.

| No. of applications.                          | Days. |      |      |      |      |      |      |      |      |       |
|---|-------|------|------|------|------|------|------|------|------|-------|
|   | 1st.  | 2d.  | 3rd. | 4th. | 5th. | 6th. | 7th. | 8th. | 9th. | 10th. |
| Soil.....                                     | 12.8  | 12.8 | 11.5 | 9.6  | 9.6  | ..   | ..   | ..   | ..   | ..    |
| " + 0.5 per cent. KCl....                     | 0.6   | 1.2  | 1.0  | 1.0  | 0.8  | 0.4  | ..   | ..   | ..   | ..    |
| " + 0.5 " " KNO <sub>3</sub> ...              | 0.45  | 1.1  | 1.2  | 0.45 | 0.4  | 0.1  | ..   | ..   | ..   | ..    |
| " + 0.75 " " CaO ...                          | 28.0  | 28.5 | 30.0 | 31.2 | 31.0 | 26.5 | 22.8 | 20.2 | 21.0 | 20.8  |
| " + 0.1 " " Na <sub>2</sub> CO <sub>3</sub> . | 4.0   | 3.6  | 3.4  | 4.4  | 3.6  | 2.6  | 2.0  | 2.2  | 1.6  | ..    |

In the case of soil alone, it will be observed that the percolation gradually decreased until it reached its limit at nine and six-tenth cc. per hour. The motion of the water doubtless moved the finer particles into the larger spaces and filled them in, thus simulating a finer grained soil. It may be that the water broke up some of the aggregates into finer particles in addition. This gradual reduction of the percolation seems to be an office of the soil in preventing the waste of this most essential element of plant growth, and it seems to be a part of a general law of nature, *that those things which are most essential to the growth of plants, as potash, lime, phosphoric acid, ammonia, and also water, the soil tends to conserve.* By comparing the percolation through the soil alone with that of the soil when one-half per cent. of potassium chloride and potassium nitrate, and 0.75 per cent. lime were present, it will be seen that the rate of percolation was in the first two instances reduced at first to one-twenty-fifth and one-thirtieth, finally to one-twenty-fifth and one-ninety-sixth, respectively, of that through the soil alone; and in the case when lime was present, the rate was more than doubled. In the case of the potassium salts the percolation slightly increased for a time, and then decreased until it was practically nil, when the observations ceased. Indeed, it took about a week for one inch head of water to pass through the soil. The percolation in the case of the lime also increased for a time, and then decreased, becoming constant at about 20.4 cc. per hour. In the case where the potassium salts were present the soil had the appearance of being puddled, which it doubtless was, while the soil containing the lime looked granular. This fact and the preceding ones, tend to show that these changes in the percolation power of the soil, is due to a change in the size of the soil particles, and would therefore persist after the salts were removed,—how long, would depend, of course, upon the subsequent treat-

ment which the soil received. Since the surface tension during percolation is zero, the above changes in the rate of percolation cannot be due to any change in surface-tension by the salts.

*Percolation after Long Standing in Contact with the Added Salts.*—When the rate of percolation was determined, the water had usually been in contact with the soil for about an hour, which was sufficient time, it was believed, for most of the compounds added, to go completely into solution. However, it was thought possible that a longer time of contact might bring about a more marked change. So after the rate of percolation was determined the first time, the excess of water was removed from above the soil, that as little as possible of the salts might be washed out, and the soil allowed to stand for eighteen days, and the rate of percolation determined again each sixth day. These determinations were made with samples of soils, to each of which was added potassium carbonate, potassium chloride, potassium phosphate, calcium oxide, and calcium sulphate. The variations due to the long standing in contact with the salts were so small, the greatest being less than three per cent., that the results need not be given here. We would conclude, therefore, that the change in rate of percolation in the soil due to the presence of certain salts is effected in less than an hour's contact with the water. The decrease in the rate of percolation previously noted being probably due to the continued motion of the water through the soil, filling the larger spaces with fine grains.

#### RATE OF PERCOLATION PER HOUR THROUGH THE SOIL ALONE AND IN THE PRESENCE OF VARIOUS SALTS.

| Sample.  | No. cc. per hour. |
|--|-------------------|
| Soil .....   | 10.2              |
| " + 0.5 per cent. K <sub>2</sub> O as K <sub>2</sub> SO <sub>4</sub> ..... | 3.6               |
| " + 0.5 " " K <sub>2</sub> O as KCl .....                                  | 1.6               |
| " + 0.5 " " K <sub>2</sub> O as KNO <sub>3</sub> .....                     | 1.8               |
| " + 0.5 " " K <sub>2</sub> O as K <sub>3</sub> PO <sub>4</sub> .....       | 3.1               |
| " + 0.5 " " K <sub>2</sub> O as K <sub>2</sub> CO <sub>3</sub> .....       | 8.9               |
| " + 0.5 " " K <sub>2</sub> O as KHCO <sub>3</sub> .....                    | 6.0               |
| " + 0.5 " " K <sub>2</sub> O as KOH .....                                  | 4.6               |
| " + 0.75 " " CaO as Ca(OH) <sub>2</sub> ,.....                             | 23.0              |
| " + 0.75 " " CaO as CaSO <sub>4</sub> .....                                | 12.8              |
| " + 0.75 " " CaO as Ca(NO <sub>3</sub> ) <sub>2</sub> .....                | 14.1              |
| " + 0.75 " " CaO as CaCl <sub>2</sub> .....                                | 18.0              |
| " + 0.75 " " CaO as CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ..... | 9.8               |

| Sample.  | No. cc. per hour. |
|--|-------------------|
| Soil + 0.75 per cent. CaO as CaHPO <sub>4</sub> .....                                | 9.4               |
| " + 0.75 " " CaO as CaCO <sub>3</sub> .....  | 8.0               |
| " + 0.5 " " MgO as MgSO <sub>4</sub> .....   | 8.6               |
| " + 0.5 " " MgO as Mg(NO <sub>3</sub> ) <sub>2</sub> .....                           | 16.6              |
| " + 0.5 " " MgO as MgCl <sub>2</sub> .....   | 8.0               |
| " + 0.5 " " MgO as MgO .....   | 9.0               |
| " + 0.5 " " MgO as MgCO <sub>3</sub> .....   | 9.0               |
| " + 0.5 " " Na <sub>2</sub> O as Na <sub>2</sub> SO <sub>4</sub> .....               | 4.1               |
| " + 0.1 " " Na <sub>2</sub> O as NaHCO <sub>3</sub> .....                            | 3.2               |
| " + 0.1 " " Na <sub>2</sub> O as Na <sub>2</sub> CO <sub>3</sub> .....               | 2.6               |
| " + 0.1 " " Na <sub>2</sub> O as NaCl .....  | 1.2               |
| " + 0.1 " " N as (NH <sub>4</sub> ) <sub>2</sub> SO .....                            | 3.4               |
| " + 0.1 " " N as NH <sub>4</sub> Cl .....  | 2.8               |
| " + 0.3 " " N as NH <sub>4</sub> NO <sub>3</sub> .....                               | 2.4               |
| " + 0.1 " " N as NaNO <sub>3</sub> .....   | 0.5               |
| " + CaO + NaNO <sub>3</sub> for 1-per cent. N .....                                  | 1.2               |
| " + 3 molecules CaO + 1 molecule NaNO <sub>3</sub> .....                             | 5.1               |
| " + 9 " " CaO + 1 " NaNO <sub>3</sub> .....  | 13.6              |
| " + 0.1 NaO as NaCl + 0.1 per cent. NaHCO <sub>3</sub> .....                         | 1.2               |
| " + Na <sub>2</sub> CO <sub>3</sub> + CaSO <sub>4</sub> .....                        | 6.8               |
| " + 1 molecule Na <sub>2</sub> CO <sub>3</sub> + 2 molecules CaSO <sub>4</sub> ..... | 9.4               |
| " frozen .....   | 22.0              |
| " " + 0.5 per cent. Na <sub>2</sub> CO <sub>3</sub> .....                            | 0.2               |

By comparing the rate of percolation through the soil to which the various salts were added, against that through the soil alone, it will be seen that all the potassium salts used have reduced the rate of percolation, the nitrate and chloride having the greatest effects; that the nitrate, chloride, sulphate, and calcium hydroxide have increased the rate of percolation, the other lime salts having little effect; that the magnesium salts have little effect, except the nitrate which has increased the percolation; that the ammonium salts used have decreased the rate of percolation much more than the potassium salts; that the sodium carbonate and chloride, and especially the nitrate, have a remarkable effect in reducing the rate of percolation. One-tenth per cent. of soda as sodium chloride has reduced the rate of percolation to one-tenth, and one-tenth per cent. of nitrogen as sodium nitrate has reduced it to one-twentieth of the rate through soil alone.

These variations are enormous, and since the greatest effects of the salts upon the percolation are not developed during the first determination, but increase as the water

continues to pass through, it is believed that these results would show that the quantities of these salts which it is practical to add to the soil would be sufficient to make a great difference in the escape of the water of the soil by percolation, and therefore in the amount of water which a soil so treated can maintain for the growth of a crop.

The soil in which there was a great reduction in the rate of percolation, due to the presence of certain salts, in each case had the appearance of being puddled, which it undoubtedly was. Slaked lime had the greatest effect in increasing the rate of percolation, which agrees with the common experience of the farmer that lime makes the soil more open and porous. It will be observed that molecular quantities of lime added to the soil to which sodium nitrate (one-tenth per cent. nitrogen) had been added, did not restore its permeability, nor did three times the molecular quantity do so. Nine times the quantity increased the permeability to about one-third more than that of the soil alone. We therefore conclude that sodium nitrate is about seven times more effective in decreasing the rate of percolation than lime is in increasing it.

It was thought desirable to know the quantitative effect of a freeze upon the rate of percolation of a soil. After determining the rate of percolation in a sample it was allowed to freeze in the soil tube, and after thawing, the vacant space all around between the soil and the soil tube was filled in with melted paraffin. The rate of percolation was then determined and was found to be a little more than double that of the soil below freezing. After this experiment enough sodium carbonate was added to the water remaining on top of the soil to give one-half per cent. sodium oxide, and the next day the rate of percolation was determined and was found to be reduced to the extremely low figure of two-tenth cc. per hour. This was a crucial test of the puddling power of the neutral sodium carbonate. It was purposed to treat small plats of a homogeneous soil with these various salts, and after several months to cut out an oblong square from the subsoil of each and determine the rate of percolation in situ by Whitney's method,<sup>1</sup> but circumstances prevented.

<sup>1</sup> Wiley's Agricultural Analysis, 1, 164.

**APPLICATION OF RESULTS TO ALKALI SOILS.**

As was to be expected from Hilgard's researches upon alkali soils, the neutral sodium carbonate is found to have a much greater effect in puddling the soil and therefore in reducing the rate of percolation, than the sodium sulphate. The sodium bicarbonate has a less effect than the neutral carbonate. The addition of a molecular quantity of gypsum to the soil containing the sodium carbonate, as was expected, had increased the rate of percolation of the soil containing the latter, but not to that of the untreated soil, for the sodium sulphate which is thus formed, itself reduces considerably the rate of percolation through the soil, while the calcium carbonate formed has very little effect in increasing it. When twice the molecular quantity of gypsum is added, the excess from the reaction with the sodium carbonate about neutralizes the puddling effect of the sodium sulphate, and brings the rate of percolation back to nearly that of the untreated soil. Hilgard has noticed that certain quantities of alkali present in a soil is highly advantageous to a crop in the semi-arid region by increasing the moisture in the soil. It seems to be one of the compensating forces of nature that the presence of the alkali in the soil, which is the result of a scarcity of rainfall, is the means of conserving for plant growth the little water which does fall.

I would suggest the following as a quick method of determining the quantity of ameliorant needed to relieve the excessive puddled condition of alkali salts: Establish as near as possible a standard for those factors which govern the soil's supply of moisture by determining the rate of capillary rise, rate of saturation, rate of percolation, rate of evaporation, etc., in those semi-alkali soils which are yielding the best crops, then by adding constantly increasing quantities of the gypsum to samples of soil from the alkali spots to be treated, the quantity required to bring the soil back to the standard may be determined to a close approximation. In this way the needs of the soil would be indicated without waiting for a year of experimentation with a crop.

**RATE OF EVAPORATION AND RATE AND HEIGHT OF CAPILLARY LIFT.**

The rate of evaporation from the soil depends upon the sur-

face area exposed and the motion, temperature, and humidity of the air, which would be approximately the same for a given surface of any soil, exposed at the same time and under the same conditions; and, also, upon the power of the soil to supply water to the surface by capillary action. In a column of soil full of water exposed to evaporation, the cavities in the soil which are full of water will give up their contents to both the large and small capillary canals which will deliver the water to the surface to meet the evaporation and plant use. As the lowering of the level of water thus proceeds, the largest capillary canals will cease one by one to deliver their water, and the rate of delivery, and, therefore, of evaporation, will gradually decrease, and the level will lower until the limit of the lift of the smallest capillary canal is reached, when the evaporation will be almost nil. In the case of a long column of air-dried soil placed in contact with water below, the rate of rise is also very rapid at first, for at first all of the capillary canals are lifting the water, the large ones very rapidly, and some of the water from the larger ones is moving laterally into the smaller canals. The larger canals, one by one, reach their limit of lift and cease to carry water, leaving the smaller and smaller ones to carry it as the capillary rise proceeds. Now the rate of rise in the smaller canals is very much slower, and some of the water from them is drawn out laterally to increase the moisture of the grains whose canals are too large to carry the water at that height. Both of these act together to reduce gradually the rate of rise of the visible capillary moisture, as the height of column increases. Both the height and rate of capillary lift will depend upon the ratio of the total amount of surface-tension acting upward (1) to the weight of the water for the height of lift; (2) to the surface area of the walls of the capillary canals, for the rate of rise. Any agent which will vary the surface-tension of the soil water, or rearrange the soil grains so as to change the shape of the capillary spaces, or change the size of the soil aggregates, will alter this ratio, and therefore the height of capillary lift, rate of capillary rise, and rate of evaporation of the soil, as well as the rate of saturation. The rate of evaporation was determined by placing twenty-five grams of the sample of soil to which the various salts had been added, in flat dishes of equal size, to each

of which enough water was added to saturate the soil, when they were weighed, set aside for evaporation to take place, and weighed each day. The dishes were shallow and the soil was about three-fourths of an inch deep. It is to be regretted that vessels of the same dimensions as the soil tubes were not at hand, for the capillary lift in these experiments is so small, and, therefore the difference in rate of ascent, that the differences in evaporation are not what they would be in deep vessels. The capillary tests were made in the usual way by filling long tubes with soil and placing them in separate vessels of water kept to a pretty constant head. The tubes used were sixty inches long and one-fourth inch bore. They were filled by attaching a small filter tube to the end of the long tube into which the soil was added, little by little, and was jolted down into the long tube by letting fall from a constant height an equal number of times. Since the soil fell into the tube at the same time it was being jolted down, the tendency to stratify, pointed out by Hilgard, was minimized. An examination showed very little stratification. These tubes were filled as nearly in the same way, and jolted as nearly the same as could be done. In order to test the uniformity of the tamping, the one containing soil alone was filled first, and after all the others were filled a duplicate was filled with soil alone. The ascent of the two was within one inch of each other. It was not possible to keep a detailed record of the rise of each ; the heights were taken after twelve and sixty days. It is to be regretted that the unexpected termination of the Louisiana Sugar School, and the unwillingness of the Experiment Station connected therewith to take up the work, terminated my observations before many of the soil columns had ceased to lift their water. However, from the two records, the comparative rate of rise may be had, and in some cases the height of lift, and is given below in inches after twelve and sixty days. The percentage of evaporation is calculated upon the total amount of water which was added, in order to saturate the air-dried soil. It is thought not worth while to give the rate of evaporation from day to day, as the ones for the day selected the third day showed the maximum differences in evaporation.

## EVAPORATION AND CAPILLARY RISE.

| Sample.  | Evaporation.<br>Per cent. | Capillary rise.<br>12 days. 60 days. |         |
|--|---------------------------|--------------------------------------|---------|
|  |                           | Inches.                              | Inches. |
| Soil alone .....   | 55.4                      | 25                                   | 45      |
| " + 0.5 per cent. K <sub>2</sub> O as K <sub>2</sub> SO <sub>4</sub> ..... | 50.14                     | 17.5                                 | 37      |
| " + 0.5 " " K <sub>2</sub> O as KCl .....                                  | 50.21                     | 15.5                                 | 32      |
| " + 0.5 " " K <sub>2</sub> O as KNO <sub>3</sub> .....                     | 48.8                      | 13.0                                 | 26.5    |
| " + 0.5 " " K <sub>2</sub> O as K <sub>2</sub> PO <sub>4</sub> .....       | 53.02                     | 17.8                                 | 34      |
| " + 0.5 " " K <sub>2</sub> O as K <sub>2</sub> CO <sub>3</sub> .....       | 55.33                     | 18.5                                 | 37      |
| " + 0.5 " " K <sub>2</sub> O as KHCO <sub>3</sub> .....                    | 56.16                     | 17.9                                 | 37      |
| " + 0.5 " " K <sub>2</sub> O as KOH .....                                  | 50.72                     | 22                                   | 38      |
| " + 0.75 " " CaO as Ca(OH) <sub>2</sub> .....                              | 50.75                     | 26                                   | ...     |
| " + 0.75 " " CaO as CaSO <sub>4</sub> .....                                | 51.72                     | 31                                   | 53.5    |
| " + 0.75 " " CaO as Ca(NO <sub>3</sub> ) <sub>2</sub> .....                | 57.81                     | 21                                   | 33      |
| " + 0.75 " " CaO as CaCl <sub>2</sub> .....                                | 50.82                     | 24                                   | 38      |
| " + 0.75 " " CaO as CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ..... | 59.93                     | 22                                   | 42.5    |
| " + 0.75 " " CaO as CaHPO <sub>4</sub> .....                               | 52.04                     | 24.5                                 | 46.5    |
| " + 0.75 " " CaO as CaCO <sub>3</sub> .....                                | 50.33                     | 28.2                                 | 57.5    |
| " + 0.5 " " MgO as MgSO <sub>4</sub> .....                                 | 49.51                     | 21.3                                 | 36      |
| " + 0.5 " " MgO as Mg(NO <sub>3</sub> ) <sub>2</sub> .....                 | 50.40                     | 21                                   | 39      |
| " + 0.5 " " MgO as MgCl <sub>2</sub> .....                                 | 54.82                     | 23                                   | 54      |
| " + 0.5 " " MgO as MgO .....   | 63.75                     | 29                                   | 47.5    |
| " + 0.5 " " MgO as MgCO <sub>3</sub> .....                                 | 64.42                     | 31                                   | 50      |

It will be observed that of the salts experimented with, potassium nitrate and potassium chloride have exerted the greatest influence in retarding both the rate of evaporation and the rate of capillary rise in the soil, and that magnesium oxide and magnesium carbonate have increased these two factors most. As a rule, those compounds which affect evaporation most affect the rate of capillary rise and in the same direction. The calcium superphosphates and the potassium carbonates are exceptions to this general rule. The hygroscopic nature of some salts would have some effect in retaining moisture *per se*, and independent of any modification of the arrangement or of the size of the soil particles, or of the surface-tension of the soil water. However, a glance at the rates of evaporation as given above, shows no changes which are proportional to the hygroscopicity of the salts used. In the column of untreated soil the capillary rise reached its limit at fifty inches in 110 days, column of soil plus the gypsum fifty-one inches in sixty-eight days, the soil plus calcium carbonate fifty inches in seventy-two days, soil plus calcium superphosphate fifty-one inches in 105 days,

soil plus magnesium oxide forty-seven inches in eighty days, and soil plus magnesium carbonate forty-seven inches in seventy days. The soil column containing potassium sulphate was still rising when it reached the end of the tube at sixty inches in 140 days. This is an increase of five inches in height over that in the untreated soil. It is most probable that those salts such as potassium chloride and potassium nitrate, which reduced the rate of rise more than potassium sulphate, would also have increased the height of lift more than did the potassium sulphate. It seems to be a general rule then that those salts which when added to a soil reduce the rate of rise of capillary moisture, increase the height of lift; and conversely that those salts which increase the rate of rise, decrease the height of lift. These variations in rate and height of capillary lift, and in rate of evaporation, do not correspond to the changes in the surface-tension of water caused by these salts, as was found to be true in the study of the rate of saturation and percolation. It is to be regretted that the rate of evaporation and the rate and height of capillary rise was not determined also in the soil to which the sodium and ammonium compounds were added, that the results might appear in this statement, but it was impossible to do so.

On account of the great length of time for the capillary moisture to reach its limit of rise, it is most desirable that an empirical formula be developed for calculating the height of lift from some easily determined factors. Since the maximum water capacity is the same as the quantity of water held in a soil column just above the level of the water which is in contact with it, and the minimum water capacity is about the same as the amount of water at the limit of the capillary rise, and since the rate of capillary rise, as determined in the soil apparatus described, gives the rate of rise for the height of column used, it seems that these three factors which are so quickly determined, together with the total height of lift, would furnish the necessary data for such a formula. It is my purpose to attempt to work out such a formula sometime in the near future.

#### GENERAL DISCUSSION OF RESULTS.

It will be noticed, in general, that the four principal factors which govern the soil's supply of moisture—the rate of satura-

tion, of percolation, of evaporation; and of capillary rise—when changed by the addition of a salt to the soil, all vary in the same direction, and oppositely, to the height of lift. This would indicate that these changes are due to a common cause. And since the soil assumed a puddled appearance in the presence of each of those salts which reduced these factors, and since sodium carbonate (which is one of that number) is known to puddle the soils, there can be little doubt that the decrease in the rates of percolation, etc., is due to a breaking up of the soil aggregates into smaller ones, and also that the increase in these factors is due to a building up of the soil aggregates into larger ones. And yet it is the common experience of chemists that the neutral salts cause the formation of aggregates and precipitate fine clay when held suspended in water, and that ammonia, caustic alkalies, and their carbonates and phosphates hinder such flocculation. While these facts apparently contradict my results, except<sup>1</sup> in the case of sodium carbonate, it must be remembered that the result in the two instances are obtained under quite different circumstances. In the one case the soil aggregates have been broken up completely; only the finest particles, almost all of which are plastic colloidal clay, are present, and they, in suspension, where they are free to move together and form aggregates large enough to settle to the bottom when salt is added to the water. Indeed all of our knowledge of the building up and breaking down of soil aggregates was obtained by the study of the behavior of soils suspended in water. In the other case, the soil mass is composed mainly of aggregates which are themselves composed of many constituents besides clay, and the fine particles are not so free to move in the water of the soil as when in suspension.

#### APPLICATION OF RESULTS TO AGRICULTURE.

It will be noticed that of the salts experimented with, those which most frequently occur in commercial fertilizers as potassium sulphate, calcium superphosphate, ammonium sulphate, etc., except sodium nitrate, would have very little effect when added in the quantities usual in practice upon the soil's supply of moisture, so their beneficial effects upon crops must be attrib-

<sup>1</sup> Wollny: Experiment Station Record, 6, No. 9, p. 766.

uted mainly to the plant-food added. But the carbonates, chloride, and nitrate of soda, have a much greater effect. While the addition of these salts would decrease greatly the rate of absorption of water, and would be of consequence in a puddled soil during a short shower, yet such a soil would become saturated during a long rainy spell—certainly during the spring rains. Then the supply of water absorbed would be more perfectly conserved in such a soil from three causes acting together, (1) the water would percolate more slowly out of the drains or out of capillary reach in the puddled soil; (2) it would rise more slowly to the surface to supply evaporation or plant growth, the delivery of the water would therefore be more constant and of longer duration; and (3) the capillary reach would be increased probably several inches, giving this much greater reservoir of ground water to draw from. Add to this the fact that the full effect of the salt added is not developed immediately (and therefore is not shown in the above analyses), and the increased puddling effect of cultivation when any of these salts are present, and it will be seen that the addition of these salts in the quantities within the reach of the farmer will be sufficient to increase considerably the soil's power to conserve its supply of moisture. Since different kinds of crops require for their highest development, according to their nature and period of growth, quite different amounts of water, a fair degree of control of the soil's power to maintain a supply of moisture, would adapt the soil to the high development of that crop (growing in that climate), which would yield the greatest financial return to the farmer. Since the rain falls at irregular periods, and there are generally times of great need of water by every crop, the ability to increase the soil's conservation power of moisture is more important than the power to decrease it; hence we have in the carbonates, chloride, and nitrate of soda, powerful agents for regulating the soil's moisture in accordance with the need of a given crop. Since water is the most essential material for plant-growth, the farmer should fertilize with regard to the soil's need of moisture as well as regards its need of plant-food. If this were done no one can predict what the increase in yield would be. In a commercial fertilizer one material often neutralizes the moisture-maintaining effect of another. For example, in kainit

the loosening effect of the gypsum would about neutralize the puddling effect of the potassium sulphate. Again, to add sodium nitrate to a soil which is too retentive of moisture by nature, to supply a deficiency of nitrogen, would actually do harm. But in the case of a soil which does not maintain enough moisture for a given crop, if the soil needs nitrogen also, sodium nitrate would give the best returns. But if this soil needed no nitrogen the carbonates or chloride of soda would remedy the moisture deficiency. These results explain why sodium nitrate gave no increased yield, even with sugar-cane, which requires an abundance of moisture upon the wet soils of Louisiana. At the Louisiana Experiment Station sodium nitrates in most cases actually decreased the yield. As was to be expected in the case of these soils, the heavy application of lime gave good returns. But lime is a very much less powerful loosening agent (about one-seventh) than sodium nitrate is a puddling agent. Lime and magnesia are the most powerful compounds found so far for decreasing the water-conserving power of soils. Doubtless a mixture of the two, easily obtained by burning a magnesium limestone, would be a still more effective agent.

Since it has been shown that in one and the same sample of soil the addition of one-tenth per cent. of nitrogen as sodium nitrate decreases the rate of percolation through the soil to more than one-twentieth of that through the untreated soil, and that the addition of 0.75 per cent. of lime has increased the rate of percolation to more than double, it is clear that the chemical composition, or the kinds and amounts of the soluble bodies of the soil have an enormous effect upon the moisture-maintaining power of a soil. This is at variance with Whitney's conclusion that the fineness of the soil particle (meaning the ultimate particle) and in general the percentage of clay determine the amount of moisture that a soil will maintain.<sup>1</sup> If he had said, "the fineness of the soil particle and the soil *aggregates*," the statement would have been more nearly correct. For it has just been shown that in a fine-grained soil containing a large per cent. of clay, certain salts can build up the particles into aggregates or the aggregates into larger ones, thus simulating an open coarse-grained soil; and other compounds can break down the

<sup>1</sup> Bull. No. 21, Nevada Experiment Station.

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aggregates into smaller ones or into the ultimate particles, making an extremely close and nearly impervious soil. The percentage of clay present is a very important factor in that it furnishes the materials for the formation of these aggregates, and the greater the quantity present, the greater the range of variation in texture possible, it would seem.

### A NEW METHOD OF EXAMINING SOILS.

By means of the improved soil instrument previously described, and from the results obtained, we have a new method for the quick examination of soils. A method which, it is believed, will give positive information concerning the moisture needs of a soil and therefore concerning the kind of crop best adapted to it, and also the kind of fertilizers or of chemical compounds to which the soil will respond most favorably in accordance with the moisture needs of a particular crop to be grown on that soil.

The results thus obtained, construed with the chemical and physical analysis of the soil, it is believed, will give enough information concerning the soil's needs, so that it will not be necessary to wait a year for field experimentation to advise the farmer as to the needs of his soil.

### A NEW LINE OF FIELD EXPERIMENTATION SUGGESTED.

The results embodied in this paper show that fertilizers or chemical compounds should be added to the soil with a regard to the soil's moisture needs as well as its plant-food needs, and especially with regard to the control of the soil's moisture, so as to meet the requirements of a given crop. I would suggest this as a profitable and fruitful line of field experimentation for the Experiment Stations to take up. In the plots thus treated with regard to the moisture needs of crops, the yield per acre, quality of crop, the temperature of the soil, the percentage of moisture the soil maintains, the rate of percolation *in situ* by Whitney's method, and the like, may all be carefully studied. This, it is believed, would extend very greatly our knowledge of practical agriculture.

All the compounds used in these experiments were chemically pure. It is my purpose, however, to try the effects of the various commercial forms of fertilizers, and of natural products singly, and in the most general combinations, upon the soil with which

I am working. The incompleteness of this report is to be accounted for by the fact that this piece of work was done during such spare time as I could find while teaching three classes with laboratory superintendence every afternoon.

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### THE RAPID ESTIMATION OF URIC ACID IN URINE.<sup>1</sup>

BY E. H. BARTLEY.

Received May 31, 1897.

THE estimation of uric acid presents well recognized difficulties, and the results obtained by any of the known methods are always open to criticism on the side of accuracy. While we admit this fact, it must also be admitted that the object for which the estimations of uric acid in urine are usually undertaken, does not require extreme accuracy. For diagnostic purposes, slight errors may usually be disregarded. Another factor often regarded by both the person afflicted and the physician, as of great importance, is the time and trouble and hence the expense to be incurred in making a correct diagnosis. The methods now in vogue for the estimation of uric acid are so time-consuming that only the chemist with a well-appointed laboratory can undertake them. This fact has prevented the mass of physicians from having such estimations made, and has deprived many unfortunate sick from the benefits to be derived from a scientific diagnosis of their ailments.

A very considerable number of methods have been proposed for the estimation of uric acid. One of the oldest methods depends upon the fact that the acid is almost insoluble in water acidulated with hydrochloric acid. The acid is set free by hydrochloric acid, and after forty-eight hours it is collected on a filter, dried at 100° C., and weighed. This method has been shown to be very unreliable, as a very considerable amount of uric acid may remain in solution. Fokker, Salkowski, and Hopkins precipitate the uric acid with ammonium chloride as acid ammonium urate, filter, wash, decompose with hydrochloric acid, let stand two hours, filter, wash, dry, and weigh on the filter. Or, the precipitated ammonium urate may be titrated with potassium permanganate, or with twentieth-normal acid. It has also been proposed to treat this precipitate with Fehling's or Pavey's copper solution, both of which are reduced by uric

<sup>1</sup> Read at the meeting of the New York Section, May 7, 1897.

acid, and thus arrive at the amount of the acid present by the amount of copper reduced. Either of these methods necessitates a rather troublesome filtration of the gelatinous ammonium urate.

Bayrac evaporates the urine to dryness, treats the residue with hydrochloric acid, washes the residue with alcohol, transfers to a special apparatus, and heats nearly to boiling with a solution of sodium hypobromite, and collects and measures the nitrogen, as in an urea determination. Haycraft precipitates the uric acid with silver nitrate in excess, in presence of ammonia, filters with the aid of a filter pump, dissolves the precipitate in nitric acid, and estimates the silver in the solution by Volhard's method, from which he calculates the uric acid.

This method has been much used, in spite of the numerous observers who have shown that the results are too high, on account of the fact that xanthin, hypoxanthin, and possibly other substances are thrown down by silver nitrate. Ludwig precipitates with an ammoniacal silver nitrate solution, in presence of an excess of magnesium mixture, filters, washes, decomposes the silver magnesium urate with sodium hydrogen sulphide, filters off the silver sulphide, evaporates the filtrate to a small bulk, acidifies with hydrochloric acid, lets the mixture stand to crystallize, filters through glass wool, washes, dissolves out any sulphur with carbon disulphide, dries at 100° C., and weighs.

This method is a modification of that used by Salkowski, but the latter<sup>1</sup> claims the priority for Ludwig's modification. Moreover, he states that hydrochloric acid does not precipitate all the uric acid from its solutions, and quotes the results of Maly and Hoffman,<sup>2</sup> who have shown the same thing. They found that silver nitrate will always precipitate some uric acid in the filtrate from the hydrochloric acid. Salkowski, in the same article, after a somewhat critical review of a number of the methods that have been proposed, declares that the methods of Haycraft, Hermann, and Czapek are all unreliable.

Salkowski claims to have been the first to propose the precipitation of uric acid by silver nitrate in an ammoniacal solution.<sup>3</sup>

<sup>1</sup> *Ztschr. phys. Chem.*, 14, 34.

<sup>2</sup> *Pflüger's Archiv.*, 6, 201.

<sup>3</sup> *Virchow's Archiv.*, 52, 61.

He then proposed to add an excess of silver nitrate, filter, acidify with nitric acid, filter, and estimate the excess of silver as chloride. Since then, he has thrown some doubt upon the constancy of composition of the silver compound with uric acid, upon which the method is based. Other authors have not all accepted this conclusion, and several have based processes upon the supposition that the composition of the double urate of silver and magnesium is a definite compound. It is admitted that the silver urate undergoes a partial decomposition during the rather tedious process of filtration and washing. Haycraft and Hermann both claim that this is not the case when the urine is treated with sodium bicarbonate and ammonia, before adding the silver solution, and hastening the filtration by means of the filter pump.

Cammerer<sup>1</sup> proposes a method in which he removes the phosphates with magnesia mixture, and then precipitates the uric acid with silver nitrate, filters, dries the residue, and estimates the nitrogen by the Kjeldahl method, and calculates the uric acid from the nitrogen found. This method avoids the following source of error in Ludwig's process. In decomposing the precipitated urate of silver with hot solution of alkaline hydrogen sulphate, a part of the uric acid is decomposed, as pointed out by Hopkins and E. Groves.<sup>2</sup> It has been proposed by several authors to estimate this acid by precipitation with a mixture of copper sulphate and sodium bisulphite, and estimation of the nitrogen in the precipitate. Arthaud and Butte have proposed a method by the use of a standard solution of cuprous thiosulphate. Martin Krüger<sup>3</sup> proposes a process based upon this principle, which he claims gives good results. Balke states that this process is not reliable when applied to the urine.

From this hasty and incomplete review of the methods that have been proposed for the estimation of uric acid in the urine, it will be seen that the processes are complicated as a rule, and the results are not in all cases reliable. As remarked above, none of these methods are rapid enough to be considered as clinical methods.

Czapek<sup>4</sup> has proposed a process intended to shorten the time

<sup>1</sup> *J. Chem. Soc.*, 56, 1040.

<sup>2</sup> *Chem. News*, 66, 107.

<sup>3</sup> *Ztschr. phys. Chem.*, 21, 311.

<sup>4</sup> *Ztschr. phys. Chem.*, 12, 502.

required. He adds to 150 cc. urine, eighteen cc. of a tenth-normal solution of silver nitrate, thirty cc. of a twenty per cent. ammonia, and fifteen cc. of magnesia mixture. The volume is now brought to 300 cc. and filtered through a large filter. Fifty cc. of this filtrate are taken for the titration, to determine the amount of silver in the solution. This is done in a flask by a solution of sodium hydrogen sulphide or potassium hydrogen sulphide. The flask is stoppered with a cork containing a small glass tube, to serve as an outlet for steam when the contents of the flask are boiled. The sodium hydrogen sulphide is added until the steam from the flask browns a strip of lead paper held before the outlet tube. The sodium hydrogen sulphide is then titrated against the silver solution in a similar manner. The amount of silver found in the filtrate, deducted from that added to the urine, gives the quantity precipitated with the uric acid. The results obtained by Czapek were good when pure uric acid was operated upon, but far from satisfactory when applied to the urine. The sources of error in this process are:

1. Too large a factor in uric acid for one cc. of the silver solution.
2. The precipitation of the xanthin bases by silver nitrate, and their calculation as uric acid, as in the Haycraft process.
3. The reduction of a part of the silver nitrate to metallic silver, while boiling the filtrate during the titration. This loss of silver is reckoned as having been precipitated with the uric acid.
4. In making up the solution to 300 cc., after precipitating the uric acid and magnesium ammonium phosphate, no account is made of the volume of this precipitate. In one trial he found the precipitate to measure seven and a half cc.

Errors 2 and 3 will be very considerable in fever urines, and in all concentrated urines, as his results show.

The author shows that the error, as compared with Ludwig's process, is from 0.002 to 0.004 gram in 100 cc. of normal urines, while in fever urines it reached in one case as much as 0.023 gram.

I have devised a process of direct titration, which I believe corrects most of these errors. The method is based upon the

complete precipitation of uric acid from the urine by silver nitrate, in the presence of an excess of magnesia mixture and ammonia, and the detection of the end reaction by potassium, sodium, or ammonium hydrogen sulphide. The titration is performed in a hot solution, to prevent the precipitation of the xanthin bases by silver nitrate.

The process is conducted as follows : To fifty cc., or 100 cc., of the clear urine, add five cc. of the magnesia mixture and about ten cc. of ammonium hydroxide (sp. gr. 0.960), or enough to give a decided excess. Warm the solution on a water-bath, and add from a burette a fiftieth-normal solution of silver nitrate. From time to time a drop is removed from the solution, by means of a dropper pipette, with a bit of absorbent cotton wound tightly over the end, so as to make an efficient filter, and after removing the cotton filter, bring it in contact with a drop of the weak sodium hydrogen sulphide solution on a white surface. Experiments with pure water, showed that it required one-half cc. of the silver solution in fifty cc., or one cc. in 100 cc., to give a marked reaction. This amount must therefore be deducted from the reading. The titration is continued until a dark ring or cloud is seen at the line of contact of the two drops, showing the presence of silver in the solution. Each cc. of silver solution corresponds to 0.00336 gram of uric acid, and the number of cc. used (less one-half cc. for each fifty cc. of urine) multiplied by this factor, gives the number of milligrams of uric acid in the urine taken. From this we may easily calculate the amount excreted in twenty-four hours, the only figure of clinical value.

As soon as the process is complete the precipitate rapidly settles, and it is best to draw off a drop or two from this clear supernatant liquid and test it carefully again. We may also check our work by running in another drop of the silver solution, to see if it produces a cloud, or to see if the precipitation be complete. As there is no excess of silver in the hot liquid at any time, there can be no reduction of silver.

If, after the titration is complete, the solution be cooled, it will usually be found that it will require from one to three cc. of the silver solution to again produce the end reaction, because of the

precipitation of the xanthin bases by the silver, in a cold solution.

This amount is usually greater in concentrated and fever urines than in normal urines, and it is this fact that invalidates Salkowski's older process, Haycraft's, Czapek's, and Denige's methods, in such urines, as they all depend upon the estimation of the excess of silver in the filtrate from the precipitated uric acid. I have found that the xanthin bases are but slightly, if at all, precipitated by silver nitrate from hot urine. It is shown in the following way:

Baginski, of Berlin, has shown that Hofmeister's method of precipitation with hydrochloric and phosphotungstic acids completely removes xanthin bodies from urine. This is confirmed by Alexander von Pohl, who, in a communication to the Paris Academy of Sciences, October 10th, 1892, uses this reaction for the quantitative estimation of leucomaines in urine. Baginski makes use of this precipitation of these bodies for their quantitative estimation. He found normal urine to contain about 0.0027 to 0.003 gram of xanthin bodies in 100 cc. of urine.

I found, by a series of trials, that the titration of a hot urine gave the same result as the same urine after the removal of the precipitate produced by hydrochloric and phosphotungstic acids, and filtered while hot. In the cold solution a part of the uric acid is also thrown down, but this is soluble in hot water, as I have also proved, by trials with solutions of pure uric acid.

I have found the difference between the hot and cold titration, in normal urines, to be usually about one cc. in fifty cc., but in abnormal urines it has been as high as three cc. If we accept the formula of the silver xanthin precipitate, as  $\text{Ag}_2\text{O.C}_6\text{H}_4\text{N}_2\text{O}_4$ , the factor for the fiftieth-normal silver nitrate will be 0.0015 gram. This would give for 100 cc.  $2 \times 0.0015 = 0.003$  gram for the average amount of xanthin bodies, calculated as xanthin. It will be seen that this agrees with the results found by Baginski. In febrile urines, and in concentrated urines the amount of these bodies is greater.

On one occasion, a specimen of morning urine passed by a healthy man, after an unusually hearty meal accompanied by some champagne, and followed by a night without sleep and

<sup>1</sup> *Ztschr. phys. Chem.*, 8, 399.

with hard work, gave a difference between the hot and cold titration of three cc. in fifty cc. of urine, instead of one cc., as on the preceding day. We have here, then, a method that gives important information outside of the quantity of uric acid. I have not had time to investigate how completely we can separate uric acid from the xanthin bases, by this process, but the results seem to point to it as a valuable clinical method, for their quantitative estimation. It has the advantage over all other methods with which I am acquainted, in that it avoids the necessity of any filtrations, and is a direct titration instead of an indirect one. It is simple, and gives good results when applied to solutions of pure uric acid. A solution of pure dry uric acid was made, with the assistance of sodium phosphate and just enough sodium hydroxide to make the solution clear, and containing one gram to the liter. Fifty cc. of this solution, containing 0.050 gram uric acid required 15 to 15.5 as the result of a number of titrations. As it took one-half cc. of the silver solution to give the reaction in fifty cc. of water, we have, after deducting this amount, 14.5 and 15 as the limits of test. This gives 0.04872 to 0.0504 as the variations in the results obtained. These results were repeated on three separate solutions. The process was then tried as follows: Fifty cc. of urine was measured out and titrated, cold, to the appearance of the end-reaction. Fifty cc. of the above solution of uric acid was then added, and the titration continued. It required sixteen cc. of the silver solution. Deducting one cc. from the result, we have fifteen cc. as the corrected reading, which agrees with the reading with the pure uric acid solution. It seems, therefore, that it is possible to estimate by this method with reasonable accuracy, uric acid in watery solutions, and to obtain good results in estimating the acid in urine to which it has been added. I regret that I have not had time to compare the result obtained by this process with those obtained with other methods. It has become general to compare new methods with Ludwig's, which gives lower results than most others. It seems to me likely that the results obtained by such a complicated process are likely to vary. The author admits that the results are about two per cent. low, and this has been confirmed by others. The

following is the result of three estimations made by my method as compared with Ludwig's:

|                                | Ludwig.<br>Gram. | Direct titration.<br>Gram. |
|--------------------------------|------------------|----------------------------|
| No. 1. Uric acid in 100 cc ... | 0.0822           | 0.08064                    |
| No. 2. " " " 100 " ...         | 0.0506           | 0.05370                    |
| No. 3. " " " 100 " ...         | 0.0684           | 0.07064                    |

The relation of uric acid to urea is generally regarded as an important guide in the determination of a normal or abnormal excretion of uric acid, and it is believed by many to be more important than a statement of the actual amount of uric acid eliminated. This ratio is variously stated as from one to thirty-three, to one to sixty. The ratio varies with the method used for the estimation of uric acid. In the above three urines the ratio was as follows:

|             | Ludwig.   | Direct titration. |
|-------------|-----------|-------------------|
| No. 1 ..... | I to 33.7 | I to 34.4         |
| No. 2 ..... | I to 37.0 | I to 34.8         |
| No. 3 ..... | I to 50.0 | I to 48.5         |

Although the number of comparative tests is too small to prove the entire reliability of the process, as compared with Ludwig's, these results indicate that it is a valuable clinical method. It is also valuable as a rapid and approximately accurate method of estimating the unoxidized xanthin bases, which have an important clinical bearing, when present in the urine in excess.

In conclusion, I would call attention to the fact, that the results by this process are more apt to be higher than the truth, than lower, on account of the difficulty of seeing the first appearance of the dark cloud, in the test. It will, therefore, be best in individual cases, for the observer to make a test of the process with a solution containing a known amount of uric acid, as a guide to the appearance of the end-reaction. With a little practice, the end-reaction can be determined with accuracy.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
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## THE ATOMIC MASS OF TUNGSTEN.

BY WILLETT LEPLEY HARDIN.

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A REVIEW of the literature on the determinations of the atomic mass of tungsten will show that a careful examination of the methods employed is of fundamental importance. Fifteen experimenters have made determinations of this constant, but with widely varying results. The method of investigation, with few exceptions, has been to reduce tungsten trioxide in a current of hydrogen at a white heat, and then to reoxidize the metal thus obtained. Deviations occur not only in the results of the different experimenters but also, with few exceptions, in the different observations of the same experimenter. Clarke<sup>1</sup> closes his summary of all the work on the atomic mass of tungsten with the following words: "Farther investigation is required in order to fully establish the true atomic weight of tungsten."

Deviations in the results of any atomic mass determination are due either to an inaccurate method or to experimental errors. It is not always an easy matter, however, to determine the source of error in a given series of variable results; but with several series of results from different experimenters, the question can be decided with a reasonable degree of accuracy. If, for instance, we have several series of results by the same method from different experimenters, and if the different series, with the exception of one, agree with each other, the probability is that the deviations in the one series are due to experimental errors. If, on the other hand, deviations occur in each series, and are more or less similar, the probability is that the method is inaccurate.

Almost every series of results on the atomic mass of tungsten, obtained by the reduction of the trioxide in a current of hydrogen, and by the reoxidation of the resulting metal, shows a variation between the maximum and minimum results of from one to two units, and in exceptional cases the deviation is much greater. In view of these facts, it seems desirable to make a

<sup>1</sup> A Recalculation of the Atomic Weights, 1897.

careful study of the method which has usually been employed in this work, rather than add to the already large number of results; for, if the method is unreliable, no experimental skill can make the results trustworthy.

The following summary will show the lack of concordance in the results of the earlier determinations:

Berzelius<sup>1</sup> was the first to determine the atomic mass of tungsten. By reduction of the trioxide he obtained the value 189.6 as a mean of two experiments for the atomic mass of tungsten. The difference between the two results was 3.0. These results and those that follow are calculated on the basis of O = 16.

Schneider,<sup>2</sup> working with material which had been carefully purified, obtained two series of results for the atomic mass of tungsten, one by the reduction of tungstic acid and the other by reoxidation of the metal.

| Reduction series.              | Oxidation series. |
|--------------------------------|-------------------|
| 184.18                         | 184.21            |
| 183.37                         | 184.16            |
| 184.01                         | 183.36            |
| 184.28                         |                   |
| 184.45      Maximum difference | 0.85              |
| <hr/>                          |                   |
| Maximum difference             | 1.08              |

The quantity of material used in these experiments varied from two to six grams.

Marchand<sup>3</sup> reduced the trioxide of tungsten and reoxidized the resulting metal; the following results were obtained for the atomic mass of tungsten:

|                    |      |             |
|--------------------|------|-------------|
| 183.91             | }    | Reductions. |
| 183.96             |      |             |
| 184.16             | }    | Oxidations. |
| 184.51             |      |             |
| <hr/>              |      |             |
| Maximum difference | 0.60 |             |

Borch<sup>4</sup> made seven reductions of tungstic acid in a current of hydrogen, and two oxidations of the metal. The results were as follows:

<sup>1</sup> *Pogg. Ann.*, 8, 1, 1826.

<sup>2</sup> *J. prakt. Chem.*, 50, 152, 1850.

<sup>3</sup> *Ann. Chem. Pharm.*, 77, 261, 1851.

<sup>4</sup> *J. prakt. Chem.*, 54, 254, 1851.

| Reductions. | Oxidations.     |
|-------------|-----------------|
| 184.10      | 184.53          |
| 182.90      | 184.32          |
| 183.77      |                 |
| 184.10      | Difference 0.21 |
| 183.03      |                 |
| 183.77      |                 |
| 183.91      |                 |

Maximum difference 1.20

The quantities of material varied from two to eight grams.

By weighing the water obtained in the reduction of tungstic acid in hydrogen, Riche<sup>1</sup> obtained the value 174 for the atomic mass of tungsten as a mean of two experiments. The difference between the two was 1.78.

Dumas<sup>2</sup> reduced the trioxide of tungsten in hydrogen and obtained the following results for the atomic mass of tungsten.

|        |
|--------|
| 184.00 |
| 183.42 |
| 184.16 |
| 183.76 |
| 183.62 |
| 184.80 |
| 184.16 |
| 184.08 |

Maximum difference = 1.38

The quantities of material varied from one to four and six-tenths grams.

Bernoulli<sup>3</sup> reduced tungstic acid at a very high temperature in a current of hydrogen. The results were as follows:

| Reduction series. | Oxidation series.         |
|-------------------|---------------------------|
| 186.78            | 186.81                    |
| 185.86            | 187.94                    |
| 186.75            | 186.77                    |
| 186.81            | 186.76                    |
| 186.70            |                           |
| 177.73            | Maximum difference = 1.18 |

Maximum difference = 9.08

The maximum difference in the two series is 10.21. He found

<sup>1</sup> *J. prakt. Chem.*, 69, 10, 1857.

<sup>2</sup> *Ann. Chem. Pharm.*, 113, 23, 1860.

<sup>3</sup> *Pogg. Ann.*, 111, 573, 1860.

that the greenish colored oxide gave the same results as did the yellow oxide.

Persoz<sup>1</sup> made two reductions of the trioxide of tungsten and obtained concordant results.

|        |  |
|--------|--|
| 183.93 |  |
| 183.94 |  |
| <hr/>  |  |

Difference = 0.01

Scheibler<sup>2</sup>, from determinations of the water in barium metatungstate, obtained the value 184.00 for the atomic mass of tungsten. Maximum difference = 1.03.

Zettnow<sup>3</sup> obtained the value 184.08 for the atomic mass of tungsten as a mean from four analyses of the tungstate of iron. From silver tungstate he obtained the value 183.80.

Roscoe<sup>4</sup> made three reductions and two oxidations of the same sample of material, beginning with 7.8840 grams of tungstic acid. The results were as follows :

| Reductions.       | Oxidations. |
|-------------------|-------------|
| 182.72            | 182.49      |
| 183.71            | 183.87      |
| 183.97            | <hr/>       |
| Difference = 1.38 |             |

Maximum difference = 1.25

From two analyses of tungsten hexachloride, Roscoe obtained the value 184.25 for the atomic mass of tungsten.

Waddell,<sup>5</sup> from carefully purified tungstic acid, obtained by reduction in hydrogen the following values for the atomic mass of tungsten :

|        |  |
|--------|--|
| 184.55 |  |
| 184.37 |  |
| 184.59 |  |
| 184.00 |  |
| 183.67 |  |

Maximum difference = 0.92

The quantities of material varied from one to four and a half grams.

<sup>1</sup> *Ann. Chim. Phys.* [4], 1, 93, 1864.

<sup>2</sup> *J. prakt. Chem.*, 83, 324, 1861.

<sup>3</sup> *Pogg. Ann.*, 130, 30, 1867.

<sup>4</sup> *Ann. Chem. Pharm.*, 162, 368, 1872.

<sup>5</sup> *Am. Chem. J.*, 8, 280, 1886.

The material used in the work of Pennington and Smith<sup>1</sup> differed from that of all the preceding experimenters, in that the last traces of molybdenum were removed by gently heating the tungstic acid in a current of hydrochloric acid gas. The method of operation was also somewhat different from those of the earlier experimenters. The metallic tungsten used in the oxidations was obtained by the reduction of tungstic acid in a platinum crucible at a white heat, in a current of hydrogen, which was conducted through the lid of the crucible. The mean of nine results from the oxidation of the metal is 184.921 for the atomic mass of tungsten. The maximum difference in the series is 0.043. The quantities of material used varied from 0.43 to 1.08 grams.

Smith and Desi<sup>2</sup> weighed the water obtained in the reduction of tungstic acid, and from that calculated the atomic mass of tungsten. The mean of six determinations is 184.704. Maximum difference 0.071.

Schneider<sup>3</sup> made a second series of reductions and oxidations. The material used in these experiments was freed from molybdenum by gently heating the tungstic acid in a current of hydrochloric acid gas. The values obtained for the atomic mass of tungsten were as follows :

| Reduction series. | Oxidation series. |
|-------------------|-------------------|
| 184.14            | 184.00            |
| 183.98            | 183.92            |
| 183.96            | 184.04            |

Maximum difference = 0.18    Maximum difference = 0.12

The quantities of material varied from two to six grams. Shinn<sup>4</sup> obtained by oxidation of metallic tungsten the following values for the atomic mass of tungsten :

|        |
|--------|
| 184.72 |
| 184.96 |
| 184.75 |
| 185.22 |

Maximum difference = 0.48

<sup>1</sup> *Ztschr. anorg. Chem.*, 8, 198.

<sup>2</sup> *Ztschr. anorg. Chem.*, 8, 205.

<sup>3</sup> *J. prakt. Chem.*, 53, 288, 1896.

<sup>4</sup> Thesis, University of Pennsylvania, 1896.

The quantities of material used varied from 0.10 to 0.22 gram of metal.

A glance at the foregoing results will show a remarkable variation. The extremely high value obtained by Berzelius is supposed to be due to the presence of alkaline impurities in the material used.

The observations of Schneider, Marchand, Borch, Dumas, and Waddell are very similar. The method of operation was the same in each case, and the material used was purified with considerable care. It is difficult to account for the variations which occur throughout these results. Molybdic acid is probably the only impurity that could have contaminated the material used in the experiments. Such an impurity would probably have lowered the separate results by the same amount, and hence would not have produced the variations. The deviations between the maximum and minimum results of the different experimenters are as follows: Schneider 1.08, Marchand 0.60, Borch 1.63, Dumas 1.38, and Waddell 0.92.

The results of Riche and Bernoulli differ widely from those obtained by other experimenters. The extremely low value obtained by the former is probably due to the method. The high results obtained by Bernoulli are more difficult to explain. The material used was carefully purified. The tungstic acid used in some of the experiments was of a greenish tinge. Some have assumed that this material was incompletely oxidized, and in this way account for the high results. Bernoulli found, however, that the greenish colored oxide and the yellow oxide gave the same results when reduced. Furthermore, neither the color of the original oxide nor the state of oxidation could affect the results obtained in the reoxidations of the metal. The results obtained by the latter method are higher than those obtained in the reductions. In view of these facts, the explanation which has been offered to account for these high results is entirely unsatisfactory.

Scheibler's results on barium metatungstate show a variation of more than one unit, and it must be added that the results obtained by the determination of the barium and tungsten in this salt were still more variable and were not used by Scheibler in calculating the atomic mass of tungsten. The two short series

of results on ferrous and silver tungstates by Zettnow are reasonably concordant.

Roscoe's experiments on the same sample of material are rather interesting. The material was reduced and reoxidized several times without being removed from the porcelain boat. The maximum difference in a series of five results is one and a half units. If the method employed by Roscoe is accurate, it is difficult to account for this variation.

The most concordant series of results on the atomic mass of tungsten is that of Pennington and Smith. The value obtained is higher than that obtained by most experimenters. Schneider<sup>1</sup> has attempted to account for the high values obtained in these experiments but, inasmuch as these results agree very closely with those obtained by Smith and Desi and Shinn, it is useless to offer an explanation for this high value until the true atomic mass of tungsten is known with greater certainty, at least until a series of concordant results has been obtained which differs from these.

Schneider's last determinations consist of two series of results, each series containing three observations. From these two short series of reasonably concordant results, Schneider concludes that the atomic mass of tungsten may be safely considered equal to 184.00. The evidence, however, is far from satisfactory. In view of the wide variations in the earlier determinations, the number of results in these experiments is entirely too small to establish anything with certainty in regard to the true atomic mass of tungsten. This fact is shown in the work of Waddell, who made five determinations. The maximum variation in the first three observations was only 0.22, while in the series of five the variation was 0.92. The same is noticed in the work of other experimenters. And in the present investigation, consisting of more than sixty determinations, a series of five concordant results were sometimes obtained, after which considerable variation was obtained. Attention will be called to this fact again in the discussion of the following observations:

#### PREPARATION OF TUNGSTEN TRIOXIDE.

The material used in the first few series of determinations was

<sup>1</sup> *J. prakt. Chem.*, 53, 283, 1896.

obtained from wolframite, from Zinnwald, Bohemia. The greenish-yellow oxide obtained by digesting this mineral for several days with aqua regia was washed with distilled water and afterwards dissolved in ammonium hydroxide. The solution was evaporated to crystallization and the ammonium tungstate which separated out was strongly ignited. The resulting oxide was again dissolved in ammonium hydroxide, the solution was evaporated to crystallization, and the resulting ammonium tungstate strongly ignited. The oxide thus obtained was placed in a porcelain boat in a combustion tube and gently heated in a current of hydrochloric acid gas to remove the last traces of molybdenum. The material was then reignited and placed in a large porcelain dish filled with distilled water. Ammonia gas was conducted into the water for several days, after which the supernatant liquid was siphoned off and evaporated to crystallization. The ammonium tungstate which separated out was ignited and the process repeated. The material obtained from the second crystallization was used in the first series of experiments.

#### REDUCTION SERIES.

Tungsten trioxide obtained by the method just described was used in these experiments. The reductions were made in a hard glass combustion tube in a current of hydrogen, which was first conducted through solutions of ammoniacal silver nitrate; potassium permanganate, alkaline lead nitrate, caustic potash, and finally through sulphuric acid and a tube containing anhydrous calcium chloride. The reduction in each case was continued for several hours at a temperature almost high enough to melt the glass tube. The porcelain boat which contained the oxide was protected from the glass tube by means of platinum foil. The weighings were made on a Troemner short-armed balance with a set of weights which had been previously calibrated. The balance is sensitive to the fortieth of a milligram. The results calculated on the basis of O = 16 are as follows :

|   | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---|-------------------------------------|------------------------|-----------------------------|
| 1 | 1.64084                             | 1.30100                | 184.05                      |
| 2 | 1.79728                             | 1.42550                | 184.044                     |
| 3 | 2.60739                             | 2.06788                | 183.98                      |
| 4 | 4.57390                             | 3.62890                | 184.33                      |

At this point an unglazed porcelain tube was substituted for the glass tube, and the reductions that follow were continued for three hours at the highest temperature obtainable in a combustion furnace.

|   | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---|-------------------------------------|------------------------|-----------------------------|
| 1 | 3.32320                             | 2.63547                | 183.94                      |
| 2 | 6.11056                             | 4.84580                | 183.91                      |
| 3 | 9.23802                             | 7.32393                | 183.66                      |

The last experiment was continued through a period of eight hours.

The first three results agree very closely and give 184.02 as a mean for the atomic mass of tungsten. The mean of the results with the glass tube is 184.10. The maximum deviation is 0.35. The mean of the results obtained with the porcelain tube is 183.84, with a maximum difference of 0.28. The maximum deviation in the whole series is 0.67.

#### OXIDATION SERIES.

The metal obtained in the foregoing reductions was used in these experiments. The oxidations were made in porcelain crucibles. The material was protected from particles of dust by means of a porcelain lid suspended a short distance above the crucible. The oxidation in each case was continued until there was no farther increase in weight.

|   | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---|------------------------|-------------------------------------|-----------------------------|
| 1 | 1.70220                | 2.14400                             | 184.94                      |
| 2 | 1.37651                | 1.73393                             | 184.86                      |
| 3 | 2.05606                | 2.58951                             | 185.00                      |
| 4 | 1.10300                | 1.38933                             | 184.91                      |
| 5 | 1.85855                | 2.34143                             | 184.75                      |
| 6 | 7.28774                | 9.18730                             | 184.15                      |

The mean of the first five results of this series is 184.89. This value is almost identical with that obtained by Pennington and Smith. The mean of the whole series is 184.77. The maximum deviation is 0.85.

#### REDUCTION OF OXIDE OBTAINED BY THE IGNITION OF METAL.

Inasmuch as the value obtained in the oxidation series is almost a unit greater than that obtained by reduction, it was

thought advisable to make a series of reductions of the oxide obtained in the series of oxidations.

|   | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten |
|---|-------------------------------------|------------------------|----------------------------|
| 1 | 2.02890                             | 1.61071                | 184.88                     |
| 2 | 2.15894                             | 1.71388                | 184.85                     |
| 3 | 2.35206                             | 1.86740                | 184.94                     |
| 4 | 1.39137                             | 1.10351                | 184.01                     |
| 5 | 1.92125                             | 1.52487                | 184.66                     |
| 6 | 1.46746                             | 1.16383                | 183.99                     |
| 7 | 5.01313                             | 3.97560                | 183.93                     |
| 8 | 6.11056                             | 4.84580                | 183.91                     |

The first three results of this series agree very closely and give 184.89 as a mean for the atomic mass of tungsten. The last three results are equally concordant and give 183.94 as the mean value. The mean of the whole series is 184.40. The maximum deviation is 1.03. The oxide used in these experiments was very light and fluffy. The material used in the last experiment was moistened and re-ignited to render it more compact.

#### OXIDATION OF METAL OBTAINED FROM THE SECOND REDUCTION.

The material obtained in the last series was used in these experiments.

|   | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---|------------------------|-------------------------------------|-----------------------------|
| 1 | 3.96360                | 4.99460                             | 184.53                      |
| 2 | 2.63034                | 3.31647                             | 184.01                      |
| 3 | 1.60964                | 2.02804                             | 184.65                      |

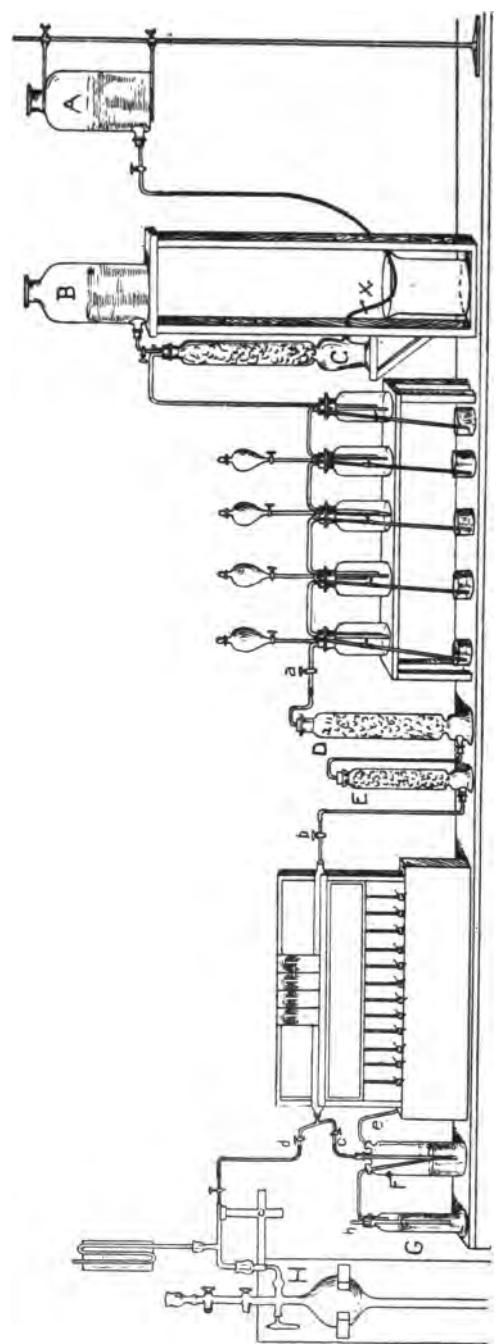
The variations in this series are similar in every respect to those of the preceding series.

In view of the wide variations in all the preceding work, an attempt was made to weigh the water formed in the reduction of tungsten trioxide. The moisture was collected in a small glass-stoppered U-tube filled with anhydrous calcium chloride. To this tube was attached another similar tube to prevent absorption of moisture from the air. Several determinations were made but the results were too discordant to establish anything. The removal of the last traces of air from the generator and wash-bottles was very difficult to accomplish, and hence the results were usually too high. The presence of air even in

small quantities would also affect the results in the reduction series. To overcome this difficulty, a different form of apparatus was constructed, the plan of which is shown in the accompanying sketch.

At the beginning of the operation, water, which had recently been boiled, was allowed to pass from the bottle *A* into the tower *C*, containing granulated zinc. When *C* was completely filled, the water passed through the small outlet tube into the first wash-bottle ; after filling this it passed into the second, and so on. When the water reached the bottom of the cork in the last wash-bottle, the stop-cock at *a* was closed. The stop-cock in each of the separatory funnels was then opened and the water allowed to rise until the stems of the funnels were completely filled. In this way the air in the generator and wash-bottles was completely displaced by water. The stop-cock at the bottle *A* was now closed and sulphuric acid allowed to drop from the bottle *B* upon the zinc in *C*, the clip at *x* being opened at the same time. The hydrogen formed by the sulphuric acid and zinc, forced the water out of *C* into the beaker below, after which the clip at *x* was closed and the clip on the siphon of the first wash-bottle opened. When the water was removed from this bottle, the clip was closed and that of the second siphon opened and so on until the water in all these bottles was displaced by hydrogen. The separatory funnels were then filled with the different solutions used in purifying the hydrogen. The stop-cocks at *a*, *b*, and *c* were opened, while that at *d* was closed ; this allowed the hydrogen to pass through the apparatus. The stop-cocks of the different separatory funnels were then opened and the solutions allowed to pass into the corresponding wash-bottles. The first bottle contained pure water, the second ammoniacal silver nitrate, the third and fourth potassium permanganate, and the fifth alkaline lead nitrate. The drying tower *D* was filled with anhydrous calcium chloride and caustic potash, and the tower *E* with alternate layers of glass wool and phosphorus pentoxide. These were substituted for sulphuric acid for, according to Dittmar and Henderson,<sup>1</sup> hydrogen when passed through sulphuric acid becomes contaminated, owing to the reduction of the acid by the hydrogen. From the drying

<sup>1</sup> Proc. Phil. Soc., (Glasgow).



towers the hydrogen passed into a thin-walled, glazed porcelain tube, placed in a combustion furnace. The bottles *G* and *F* acted as a regulator; the outlet to *F* was connected to a suction tube *e*. When the suction was greater than the backward pressure of the wash-bottles, air passed in at *h* and through the columns of sulphuric acid in *G* and *F*. The length of these two columns of acid were adjusted so that the pressure exerted against the air passing through them was equal to the backward pressure of the wash-bottles. The Sprengel pump *H* was attached so that the metal might be cooled in a vacuum and thus prevent any occlusion of hydrogen. When the reductions were complete the stop-cocks at *b* and *c* were closed. The reservoir of the vacuum pump was exhausted and the stop-cock at *d* opened. This was repeated several times, until the vacuum was almost perfect.

This form of apparatus was used in all the reductions which followed. The air could be completely removed from the apparatus in a short time. The reductions were continued for a period of three hours at the highest temperature obtainable in a combustion furnace. When the quantity of material exceeded three grams the time was longer.

#### REDUCTION SERIES.

All the material resulting from the preceding experiments was ignited and digested for several days with pure aqueous ammonia. A residue was left, which gave the bead test for silica. It is evident from this, that tungstic acid, when reduced in a porcelain boat, takes up silica. The solution of ammonium tungstate was siphoned off and evaporated to crystallization. The crystals of ammonium tungstate were strongly ignited, and the resulting oxide used in the experiments. For the first time the metal was allowed to cool in a vacuum.

|         | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten |
|---------|-------------------------------------|------------------------|----------------------------|
| 1 ..... | 3.55192                             | 2.81560                | 183.55                     |
| 2 ..... | 4.59362                             | 3.64461                | 184.34                     |
| 3 ..... | 4.30435                             | 3.41459                | 184.21                     |
| 4 ..... | 2.64671                             | 2.09900                | 183.95                     |

The mean of these four results is 184.01. The maximum difference is 0.79.

## OXIDATION SERIES.

The metal obtained in the preceding series of results was re-oxidized, and the following values obtained for the atomic mass of tungsten :

|         | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|------------------------|-------------------------------------|-----------------------------|
| 1 ..... | 2.80958                | 3.54370                             | 183.70                      |
| 2 ..... | 3.63095                | 4.57662                             | 184.30                      |
| 3 ..... | 2.09740                | 2.64455                             | 183.99                      |

This series, like the preceding, is of little value, owing to the wide variation in the results.

Inasmuch as the removal of air from the present form of apparatus was a matter of little difficulty, another attempt was made to collect the water formed in the reduction of tungsten trioxide, and from its weight calculate the atomic mass of tungsten. The moisture was collected in a glass-stoppered U-tube filled with alternate layers of glass wool and phosphorus pentoxide. From a series of blank experiments, it seemed that any error introduced by the presence of air in the apparatus would be almost inappreciable. The following results were obtained :

|         | Weight of $\text{WO}_3$ .<br>Grams. | Weight of $\text{H}_2\text{O}$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|-------------------------------------|--|-----------------------------|
| 1 ..... | 5.01313                             | 1.16742                                    | 184.07                      |
| 2 ..... | 2.02890                             | 0.47090                                    | 184.86                      |
| 3 ..... | 7.04192                             | 1.63864                                    | 184.27                      |
| 4 ..... | 3.34204                             | 0.77832                                    | 184.07                      |

The variations in this series are similar in every respect to those of the different reduction and oxidation series.

The next line of investigation was to make a number of determinations with material obtained from different minerals and different localities.

#### REDUCTION OF TUNGSTEN TRIOXIDE OBTAINED FROM SCHEELITE FROM NEW ZEALAND.

The oxide was extracted from this mineral and purified in a manner similar to that described under wolframite. No trace of molybdenum was found even before the oxide was heated in hydrochloric acid gas. The results of seven reductions are as follows :

|   | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---|-------------------------------------|------------------------|-----------------------------|
| 1 | 3.41018                             | 2.70410                | 183.83                      |
| 2 | 2.99000                             | 2.37084                | 183.80                      |
| 3 | 3.11613                             | 2.47047                | 183.67                      |
| 4 | 4.32830                             | 3.43118                | 183.56                      |
| 5 | 4.66735                             | 3.70050                | 183.72                      |
| 6 | 4.29620                             | 3.40623                | 183.71                      |
| 7 | 3.39104                             | 2.68885                | 183.80                      |
| 8 | 2.93215                             | 2.32515                | 183.87                      |

The mean of this series is 183.745. The maximum deviation is 0.20. Considering the number of experiments, this is the most concordant series of results ever obtained by reducing the trioxide of tungsten and weighing the resulting metal. In experiments 2 and 7, the metal was cooled in a vacuum; in all the other experiments it was cooled in hydrogen.

#### OXIDATION SERIES.

The metal obtained in the preceding reductions was used in these oxidations. The results of six experiments are as follows:

|   | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---|------------------------|-------------------------------------|-----------------------------|
| 1 | 2.70219                | 3.40775                             | 183.83                      |
| 2 | 2.36771                | 2.98620                             | 183.75                      |
| 3 | 2.46705                | 3.11016                             | 184.13                      |
| 4 | 3.42163                | 4.31472                             | 183.90                      |
| 5 | 3.40086                | 4.28890                             | 183.82                      |
| 6 | 2.68249                | 3.38145                             | 184.20                      |

This series gives a mean of 183.94, with a maximum difference of 0.45.

#### REDUCTION OF TUNGSTEN TRIOXIDE OBTAINED FROM WOLFRAMITE FROM CONNECTICUT.

The oxide was obtained from this mineral and purified by the method already described. The details of the work were the same as in similar series which precede. The results were as follows:

|                           | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---------------------------|-------------------------------------|------------------------|-----------------------------|
| 1                         | 3.14520                             | 2.49330                | 183.58                      |
| 2                         | 3.10516                             | 2.46141                | 183.51                      |
| 3                         | 4.17792                             | 3.31244                | 183.83                      |
| Mean = 183.64             |                                     |                        |                             |
| Maximum difference = 0.32 |                                     |                        |                             |

## OXIDATION SERIES.

The metal was obtained from the preceding reactions.

|         | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|------------------------|-------------------------------------|-----------------------------|
| 1 ..... | 2.48088                | 3.12790                             | 184.05                      |
| 2 ..... | 2.44588                | 3.08318                             | 184.22                      |
| 3 ..... | 3.29370                | 4.15260                             | 184.06                      |

The mean of these results is almost one-half a unit greater than the mean of the reduction series. It seems that the results from oxidations are invariably higher than those obtained by reduction.

## EXPERIMENTS ON MATERIAL OBTAINED FROM HUBNERITE FROM COLORADO.

The usual method of purification was used. Two reductions of the trioxide gave the following results:

|         | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---------|-------------------------------------|------------------------|-----------------------------|
| 1 ..... | 1.83600                             | 1.45618                | 184.03                      |
| 2 ..... | 4.31878                             | 3.42450                | 183.81                      |

The metal resulting from these reductions was reoxidized.

|         | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|------------------------|-------------------------------------|-----------------------------|
| 1 ..... | 1.45184                | 1.83090                             | 183.85                      |
| 2 ..... | 3.40470                | 4.29225                             | 184.14                      |

## EXPERIMENTS ON MATERIAL OBTAINED FROM SCHEELITE FROM BOHEMIA.

The oxide was extracted and purified by the usual method. Two reductions were as follows:

|         | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---------|-------------------------------------|------------------------|-----------------------------|
| 1 ..... | 2.77363                             | 2.19950                | 183.89                      |
| 2 ..... | 2.13327                             | 1.69120                | 183.63                      |

The reoxidation gave:

|         | Weight of W.<br>Grams. | Weight of $\text{WO}_3$ .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|------------------------|-------------------------------------|-----------------------------|
| 1 ..... | 2.18985                | 2.76060                             | 184.17                      |
| 2 ..... | 1.68208                | 2.12070                             | 184.08                      |

Throughout this work, it had been noticed when tungsten trioxide was heated in a current of hydrochloric acid gas for some time that a considerable sublimate was formed, even when

molybdic acid was absent. Enough of this sublimate for an atomic mass determination was obtained as follows: Tungsten trioxide was heated for some time in a current of hydrochloric acid gas at a temperature of about 400°. The sublimate was removed from the tube, strongly ignited, and gently reheated in a current of hydrochloric acid gas. The small white sublimate formed did not respond to the test for molybdic acid. The portion left in the porcelain boat was removed from the tube and strongly ignited in the air for a period of ten hours. It was then reduced in a current of hydrogen and the following result obtained:

|         | Weight of $\text{WO}_3$ .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---------|-------------------------------------|------------------------|-----------------------------|
| I ..... | 1.12970                             | 0.89610                | 184.13                      |

Upon reoxidation, this metal gave 184.87 for the atomic mass of tungsten.

The results from the sixty-four determinations made in the present investigation, show a maximum deviation of one and a half units. A discussion of these results, with a view of arriving at the true atomic mass of tungsten, would be useless. To take the mean of all the results would be entirely unsatisfactory, and yet there seems to be no reason why any one result should be accepted in preference to any other. It will be noticed, in several instances, that three or four consecutive results agree very closely. These different series of concordant results, however, do not agree. The variations in these results are similar in every respect to those in the results of earlier experiments.

Various causes suggest themselves as possible factors in producing these variations. The lower values obtained in the latter part of the investigation are undoubtedly due to a better form of apparatus and a higher temperature.

The reductions were all made in a porcelain boat. During each determination the boat increased in weight by from one to three milligrams. It is difficult to determine whether this absorption of tungsten by the boat would affect the results or not. If the tungsten is absorbed as metal it would produce no effect on the results, if not absorbed as metal it would. It was shown in the first part of this investigation that the metal obtained in the reductions contained silica. This may, in part,

account for the higher values obtained in the oxidations. In view of these objections to the use of porcelain, a series of reductions were made in which a platinum boat was used. This, however, did not remove the difficulty; platinum absorbs tungsten and tungsten absorbs platinum, and the results obtained were just as variable as those obtained with the porcelain boat.

A series of observations on tungsten trioxide was next made with a view of determining whether or not this compound is suitable for atomic mass determinations.

The first point was to determine how rapidly this compound takes up moisture from the air. Several series of observations were made, and it was found in each case that the absorption of water was inappreciable. The rate at which the water was absorbed is best shown by the following series of weighings of tungsten trioxide, which had been left for several days in the open air. The oxide was first strongly ignited, then placed in a porcelain boat, carefully protected from dust, and left for four days in an open window.

|  | Grams.  |
|--|---------|
| Weight of the oxide at the beginning ..... | 5.34600 |
| "    after one day.....                    | 5.34605 |
| "    "    two days .....                   | 5.34620 |
| "    "    three days.....                  | 5.34625 |
| "    "    four days.....                   | 5.34630 |

From these observations it is evident that no appreciable error can be introduced by the absorption of moisture during the weighing of this compound.

A series of observations was also made to ascertain the action of light on this oxide. A weighed quantity of the material was placed in a desiccator and left for some time in direct sunlight. Weighings made at different intervals showed that no reduction had taken place. In working with this compound, it is unnecessary to cover the desiccator with a black cloth.

Upon examining the porcelain tube after a reduction, a slight sublimate was usually noticed. Whether the tungsten trioxide is volatile at that temperature, or whether the moisture formed in the reduction carried mechanically small particles of the oxide from the boat, was not determined. In either case an error is introduced, but in all probability a very small one.

A series of observations was next made to determine whether

or not tungsten trioxide contains nitrogen. A number of reductions were made in the usual way and the products set free were conducted through a U-tube containing pure water and a few drops of Nessler's reagent. The oxide used was obtained by strongly igniting ammonium tungstate for two days. Hydrogen was allowed to pass through the reduction apparatus for some time in order to completely remove the air. When the reduction was started, the solution in the U-tube began to assume a yellowish color, even when the temperature was comparatively low. Before the reduction was half completed, the solution was of a deep yellowish brown color. In some instances a slight precipitate was formed at the surface of the solution. Several observations were made, and the ammonium test distinctly obtained in each case. A series of blank experiments were made and no coloration was produced. The experiments proved conclusively that the oxide obtained by the ignition of ammonium tungstate contains nitrogen. No attempt was made to determine the quantity of nitrogen present. The oxide obtained by the ignition of metal was also examined and found to contain a trace of nitrogen. Whether the nitrogen in the former oxide was present as an oxynitride or as an ammonium residue, was not determined. If it exists as an ammonium residue, then hydrogen must also be present. A number of experiments were made by fusing the oxide with lead oxide and also with anhydrous sodium carbonate, with a view of converting any hydrogen present into water. Nothing definite was established, but there were some indications that a small quantity of water was formed. If the nitrogen is present in large enough quantities to affect the atomic mass determinations, it would probably lower the results and also produce variations, for it is not likely that the quantity would be the same in all cases.

In regard to the occlusion of hydrogen by the metal, nothing definite was established. The results obtained by cooling the metal in a vacuum were practically the same as those obtained when the metal was cooled in hydrogen.

It has been shown in the foregoing observations, that tungsten attacks the vessels in which the atomic mass determinations have been made, that the oxidation of tungsten is either slightly volatile, or that a small portion is carried mechanically by the

water formed in the reductions, and that the supposed trioxide of tungsten contains nitrogen and probably hydrogen. In view of these facts and of the fact that there is no means of determining when the reduction of oxide to metal is complete, and finally, in view of the fact that more than one hundred and fifty determinations have been made of this oxide, and nothing definite established, it is evident that the method usually employed in the determination of the atomic mass of tungsten must be regarded as unsatisfactory.

UNIVERSITY OF PENNSYLVANIA.

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#### OBITUARY.

Mr. CARL H. SCHULTZ was born at Jutroschin-on-the-Orla, in the Province of Posen, on the 2nd of October, 1827. He began his education at the schools of his native town. In 1840 he entered the schools at Krotocchin, and later the gymnasium of Lissa. From there he went to the University of Breslau, from which he graduated in 1849. Being particularly fond of chemistry and natural philosophy, he continued the study of these branches for some time after the regular course was finished.

While in the tertiary course in the gymnasium, although only thirteen years of age, he gave private instructions in mathematics and later in chemistry.

In 1853, during the World's Fair in New York, he came to America, bringing with him very little money, but some strong letters of recommendation, and was not long in finding employment. His first situation was with the late Professor Benjamin Silliman, who had charge of the Chemical Department of the Exposition. Later he was appointed assistant to Dr. John Torrey, Professor of Chemistry at the College of Physicians and Surgeons, then in Crosby street. In 1854 the United States Assay Office appointed Dr. Torrey Chief Assayer, and he at once made Mr. Schultz his assistant. He not being a citizen of the United States was offered as an objection to his appointment, but he overcame this by taking out his first papers, and after the proper time, his second papers. Few men ever felt prouder of their citizenship or could have been more thoroughly American.

While at the Assay Office, besides his routine work of making

gold and silver assays, he found time to do a good deal of investigation in connection with Dr. Torrey, and much valuable work toward improving the methods of assaying. At the same time he did the chemical work for the Manhattan Gas Company,



and the laboratory at 18th Street Station was fitted up under his supervision, and remains to-day, with few alterations, as he left it.

While holding the position at the Medical College in Crosby Street, he lodged in the college building and took his meals in a boarding house in the neighborhood. There he met the late

Thomas Warker, who showed him a French siphon. With his characteristic quickness of perception, he at once saw its advantages for keeping water fresh and sparkling, and especially its value in the sick-room. Believing that the manufacture of artificial mineral waters would be a profitable industry, he began making investigations on the subject.

In 1862 he and Thomas Warker established a business for the production of mineral waters on a small scale, under the firm name of Schultz and Warker, which continued until 1871, when Mr. Schultz bought out Mr. Warker's interest, and has since conducted the business under his own name. In 1871 the business had assumed such proportions that it was necessary to move into larger quarters, and he purchased property on First Avenue and located his factory where the business is still continued.

In 1867 he was sent to Europe to examine into the methods of assaying employed by foreign governments, and on his return he submitted a report, many of the recommendations of which were adopted.

In 1872, after seventeen years of service, he resigned from the Assay Office and also from the Manhattan Gas Co., although he was afterwards many times called upon in consultation in regard to questions of great importance. General Roome, President of the Gas Co., once remarked that Dr. Schultz's opinion was of special value to them, because it carried with it not only thorough scientific knowledge, but sound business judgment as well, and no matter how much pressure was brought to bear upon him, he would not endorse anything until satisfied by investigation of its merit.

As an illustration of his untiring industry and genius for application, I might mention, that for a number of years after establishing his business, he still retained his position in the Assay Office and remained chemist to the Gas Co., any one of which posts would be regarded by many men as quite sufficient for the employment of all their energies.

He was very fond of chemical work, and often regretted that he had not more time to devote to it, and those who have visited the factory, will agree with me that his laboratory is the finest and best equipped in the country. It was fitted up without the slightest regard to expense, and with no restrictions

whatever on apparatus or supplies. What a boon it would be to our profession if more of our employers took so much interest in science and provided their chemists with every facility for work.

He was a genial and companionable man, cordial and friendly to all to a degree seldom met with. Especially marked was his consideration and sympathy for those in his employ. His men came to feel that in him they had a good and true friend who would not forsake them, a feeling justified by his many benefactions.

Naturally of a charitable disposition, he not only contributed liberally to public charities, but his private benefactions were both numerous and judicious. Many a man would never have attained the position he now holds, had it not been for Mr. Schultz's timely assistance.

The most lovable side of the man was best seen in his home and in his social relations. He and his wife were most genial hosts and most lavish entertainers when they resided in 140th street, and later at their beautiful home in Murray Hill. He leaves a wife, ten children and seven grandchildren to mourn his loss. The funeral was held at his late residence in Murray Hill on May 31st. The interment was in Long Hill Cemetery, near Summit, about three miles from his home.

Mr. Schultz was a member of the American Chemical Society, New York Academy of Sciences, the College of Pharmacy, the American Association for the Advancement of Science, the Reform Club, and all the prominent German Clubs in this city.

Mr. Schultz was a man of keen insight, sound judgment, and affectionate and generous disposition. To be counted among his friends was an honor and a privilege. A. P. HALLOCK.

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#### NOTE.

*Hydrolysis of Starch by Acids.<sup>1</sup>—An Apology.*—It has recently been brought to our notice that in 1880 and 1881<sup>2</sup> Prof. H. W. Wiley demonstrated that a practically constant relation existed between the optical and copper-reducing constants in samples of commercial glucoses investigated by him. We wish to apolo-

<sup>1</sup> This Journal, 18, 869, 900.

<sup>2</sup> Proc. Am. Assoc. of Sci., 1880 and 1881.

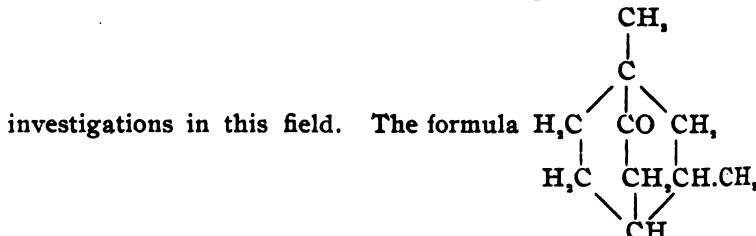
gize to Prof. Wiley for our neglect to refer to his work, and state that the unintentional omission was made because the presumably complete bibliographies consulted by us made no mention of these papers.

GEO. W. ROLFE,  
GEO. DEFREN.

### NEW BOOKS.

**TRAITÉ DE CHEMIE ORGANIQUE D' APRÈS LES THÉORIES MODERNES.** By A. BEHAL. Tome Second. pp. 1056. Paris: Octave Doin. Price 17 francs.

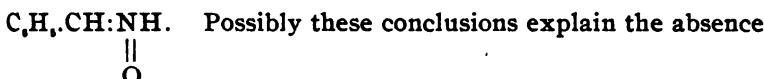
The general merits and excellencies of this work were pointed out in the review of the first volume;<sup>1</sup> these are maintained in the present and concluding portion. A clear demonstration of the structure of benzene is first given, so far as the presence of a closed chain and the number and nature of isomeric derivatives are concerned. Of the various expressions which have been suggested for its representation, Kekulé's is, after discussion, preferred. The section dealing with cyclopolymethylenes comprises 125 pages, of which 80 are devoted to the terpenes; this portion is fully equal to the high expectations inspired by the author's



is provisionally assigned to camphor for reasons given. It would have been well to have also shown Bredt's formula as a possible alternative. v. Baeyer's system of nomenclature is employed in this section, and also his plan of distinguishing isomers. In connection with the benzaldoximes, Hantzsch and Werner's theory of stereoisomerism is examined in detail and rejected on the following grounds: (1) It indicates the existence of stereoisomeric derivatives of trivalent nitrogen atoms, such as C<sub>6</sub>H<sub>5</sub>CH:NC<sub>6</sub>H<sub>5</sub>, which are unknown in spite of special efforts to obtain them. (2) It supposes that certain radicals in the molecule may both attract and repel one another without any previous

<sup>1</sup> This Journal, 19, 437.

chemical changes occurring in the compound. (3) It does not accord with the formation of two isomeric derivatives by the introduction of a radical into the molecule of  $\beta$ -benzaldoxime, although such compounds are known. The author represents  $\alpha$ -benzaldoxime by the ordinary formula  $C_6H_5CH:NOH$ , and the  $\beta$  compounds by one or other of the formulas  $C_6H_5CH.NH$ ;



of reference to Hantzsch's extension of his conception of stereoisomerism to diazo compounds, and of his controversy with Bamberger on the constitution of these and similar substances. As in the first volume, so in this, there are certain omissions which are difficult to understand, and which it would appear hard to justify; for example, Claisen's name is not recorded in connection with the isoxazoles, nor is reference made to his work and Nef's on the constitution of di- and triketones, such as dibenzoylmethane and tribenzoylmethane, which are simply represented by the keto formulas, nor is the isomerism which has been observed in this series of compounds mentioned. The alkaloids are classified according to the plant from which they originate; in the present state of our knowledge this is decidedly commendable, but the omission of W. Koenig's name in connection with the quinine group, and of Schunk's in connection with chlorophyll, is scarcely equitable, whilst A. G. Perkin's investigations of the constitution of natural coloring matters has not been confined to mallotoxin (rottlerine), as might be inferred. The "salt formation" is given in explanation of the action of phenol phthalein as an indicator. The electrolytic dissociation theory offers a much more probable solution of the phenomena. The volume concludes with a copious index to both parts of the work.

J. B. T.

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#### BOOKS RECEIVED.

Commercial Fertilizers. Special Bulletin, May, 1897. H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. 8 pp.

1. General Discussion on Commercial Fertilizers. 2. Analyses of Fertilizing Materials sent on for Examination. 3. New Fertilizer Law.

Bulletin No. 45, March, 1897. 16 pp. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

The Habits, Food, and Economic Value of the American Toad. Bulletin No. 46, April, 1897. 30 pp. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

On Field Experiments with Tobacco in Massachusetts. Bulletin No. 47, April, 1897. 31 pp. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

A Handbook on Modern Explosives. By M. Eissler. Second edition, enlarged. 150 illustrations. xx + 406 pp. London: Crosby, Lockwood & Son; and New York: D. Van Nostrand Co. Price, \$5.00.

The San José Scale in Kentucky. Bulletin No. 67. 17 pp.; Analyses of Commercial Fertilizers. Bulletin No. 68. 13 pp. May, 1897. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

Twentieth Annual Report of the Connecticut Agricultural Experiment Station for 1896. Agricultural Experiment Station, New Haven, Conn. xvi + 414 pp. Report of Station Staff on Food Products; Their manufacture and sale; Maple syrup and maple sugar; Sugars; Syrup; Honey; Lard; Pepper; Mustard; Cheese; Coffee; Milk; Cream of tartar, and cereal foods, and laws regulating foods and drugs; Fertilizers; Connecticut fertilizer law; Sampling; Miscellaneous analyses and reports; Availability of nitrogen; Experiments with forcing house crops, tomatoes, radishes, carnations, and cucumbers; Blight, burn or scald of tomato plants; Insect notes; Prevention of potato scab; Leaf blight of melons; Fungus of peach scab; Shelling of grapes; Experiments in growing tobacco with different fertilizers; Nitrogen, phosphoric acid and potash in peas and beans; Observation on the growth of maize continuously on the same land for nine years; Effects of minute quantities of acid on the solubility of globulin in salt solutions; Proteids of lupin seeds; Sunflower seeds; Cow pea; White podded adzuki bean, and maize kernel.

An Electrical Method of Determining the Moisture Content of Arable Soils. By Milton Whitney, Frank D. Gardner, and Lyman J. Briggs. Bulletin No. 6, U. S. Department of Agriculture, Division of Soils. 26 pp. Washington: Government Printing Office.

The Chlorination Process. By E. B. Wilson, E.M. v + 125 pp. New York: John Wiley & Sons. Price, \$1.50.

#### ERRATA.

Page 552 (July number), line 12, for "zinc ammonium sulphate" read "zinc ammonium phosphate."

Page 587 (July number), line 3 from bottom, for "+" read "—."

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AMERICAN CHEMICAL SOCIETY.

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ON THE SPEED OF REDUCTION OF FERRIC ALUM BY  
SUGAR.

By J. H. LONG.

Received July 7, 1897.

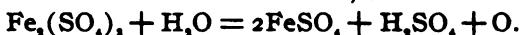
In two papers published last year in this Journal, I gave numerous experiments on the inversion of cane sugar solutions by various salts. In several cases certain secondary reactions were noticed, but they were not discussed at length, as they had no direct bearing on the problem in hand. Certain salts were found to invert sugar and to become reduced or otherwise changed at the same time. A good illustration of this is a mixture of ferric alum and sugar, in which inversion of the sugar and reduction of the iron salt take place rapidly on warming, and even on standing in bright sunlight through several warm days. A somewhat analogous change takes place with solutions containing chrome alum, but this was not followed in detail.

On June 4, 1896, a solution was prepared containing in 250 cc., fifty grams of pure cane sugar and ten grams of ferric alum; this had the usual dark color. It was allowed to stand in the light two weeks. At the end of the first week the color had changed to light green, with apparent conversion of the ferric to ferrous salt. On June 18, a polarization was made, giving  $\alpha = -3.85^\circ$  in a 100 mm. tube, at  $20^\circ$ . A test made some days later showed the same results. This doubtless corresponds to complete reduction, as the theoretical end reading of  $-4.3^\circ$  is not reached in such a mixture, as I pointed out in my papers referred to, and possibly from an alteration of a little of the levu-

lose. The solution was found also to contain free sulphuric acid, and an approximate titration showed this to correspond in amount to what should be expected from a conversion of ferric into ferrous sulphate. It is not possible here to measure the rate of inversion, because of the dark color of the liquid, until near the end, and this was not attempted.

At first sight it appeared possible to measure the rate of reduction of the ferric salt from the change of color during the reaction, but this was not found satisfactory, even by the aid of an excellent spectro-photometer, and the conversion of the ferric salt into thiocyanate. Two reasons may be given for this; it is well known that the color of a ferric solution varies greatly with the temperature, and this alone makes an accurate observation difficult with the ordinary instruments; further, it has been shown by Krüss that no accurate relation exists, in the case of ferric thiocyanate, between concentration and extinction coefficient. My own experiment confirms this view.

As may be easily seen, the usual methods of determining ferric in the presence of ferrous salts can not be applied here, because of the presence of the great excess of organic matter, and I therefore gave up all attempts to make direct determinations. On consideration of the reaction which must take place in the reduction, however, a possible method soon presented itself, and this on trial was found to be very satisfactory. Considering the iron salt alone in the alum, the reaction is this:



Ferrous sulphate and free sulphuric acid are formed and remain in solution, while oxygen is liberated and is absorbed in the oxidation of a part of the sugar.

The text-books are practically silent on the subject of the oxidation of sugar by heavy salts in neutral or acid solution. Even less seems to be known concerning the products of such oxidation than is known for the Fehling and similar reactions in the presence of alkali. In an experiment on the subject, the following observations were made: I dissolved fifty grams of pure cane sugar in water and mixed with it fifty grams of ferric alum in solution; the mixture was diluted to 250 cc. and heated in a flask with a capillary stopper to 85° C. In about an hour the color of the liquid had become greenish, indicating reduc-

tion to the ferrous condition, but on longer heating the solution grew darker and became finally dark brown. During the last stage of the heating numerous gas bubbles escaped from the liquid, suggesting active decomposition. With lime water these bubbles gave a precipitate. In a second similar experiment the apparatus was arranged to permit the collection of this gas. For this purpose a sulphuric acid bulb was attached to the delivery tube from the flask, and beyond this a weighed potash bulb. After the evolution of the gas had ceased the increase of weight in the potash bulb was found to be 0.015 gram. Although this amount is not large, it is sufficient to indicate that a small portion of the sugar undergoes advanced oxidation. What the principal changes are lies outside the scope of this investigation.

If, as suggested above, a direct reduction of the ferric salt is effected, the change is one which should be easily followed by a series of electrical conductivity determinations, and this hypothesis I was soon able to confirm by simple experiments. With decomposition of the complex ferric salt into the simpler ferrous salt and free acid a marked increase in conductivity should be noticed, and that this is the case, the following experiment shows. I made up a thick syrup with ferric alum and determined its resistance in a  $\parallel$  cell of the Kohlrausch type at  $20.2^\circ$ , and found it to be 406 ohms. After standing several days in January, in diffused light, I found at  $20^\circ$  407.5 ohms; that is, practically, no change. I next heated the solution through five hours to a temperature of  $70^\circ$  in a flask closed with a rubber stopper and long capillary tube. After cooling a new test was made, showing now a resistance of 197.2 ohms at  $20^\circ$ .

Another solution was made containing in 500 cc. fifty grams of sugar and 48.2 grams of pure ferric alum. The resistance of this was found to be 396.6 ohms at  $20.3^\circ$  in the same apparatus. A portion of this solution was allowed to stand four months exposed to the light, when a new test was made. It was then green in color, but still contained a little ferric salt. The resistance at  $20^\circ$  was found to be 199.5 ohms. Part of the same solution stood through the same period in a dark cupboard and at a higher mean temperature. It remained yellowish brown, and gave in the same apparatus a resistance of 323.3 ohms at  $20^\circ$ .

The influence of the light is very clearly indicated by the above tests.

As is well known, dilute solutions of ferric alum are not stable, even at the ordinary temperature, while relatively strong solutions decompose when heated. To follow the rate of reduction accurately, it is desirable to choose such a concentration and such a temperature that the whole change may be completed in a single working day, that is, within eight or ten hours. A mixture containing 15.0625 grams of ferric alum and 100 grams of sugar in 500 cc. was tried, but as it became turbid at 70°, after a time, was discarded. The same was found true of the solution, referred to above, containing in 500 cc. 48.2 grams of alum and fifty grams of sugar. It was found practically that the most stable solutions were those made with large amounts of ferric salt, the weight of sugar present being of far less importance. After a few trials the following solution was found to have the required stability and to satisfy all demands: Ferric alum, 120.05 grams; sugar, 100 grams; water to make 500 cc. This is a fourth normal solution, as it contains one molecule of alum in four liters. Many of the following experiments were made with a solution of this concentration. It was found to have a resistance of 282 ohms at 20° in the cell used throughout all the tests; this corresponds to a molecular conductivity,  $10^3\mu = 111.4$ , the factor for reduction being determined by fiftieth-normal potassium chloride and saturated sodium chloride solutions. The following table shows the variation in the value of  $\mu$  with dilution:

TABLE I.

| V, liters. | $10\mu^3$ . |
|------------|-------------|
| 4          | 111.4       |
| 8          | 179.5       |
| 16         | 248.5       |
| 32         | 318.0       |
| 64         | 388.1       |
| 128        | 467.5       |
| 256        | 567.0       |
| 512        | 692.3       |
| 1024       | 846.4       |
| 2048       | 1093.5      |

The solutions became somewhat turbid before the end of the experiments, which were conducted as rapidly as possible. The

last values show that dissociation was far from complete. When a portion of the undiluted solution was heated to 75° through five hours, it became yellowish green and completely reduced. The resistance for this was found to be 126.6 ohms, corresponding to  $\mu = 248.1 \times 10^{-3}$ , for the original ferric salt. On diluting the product the conductivities were found as shown in the table below, the dilution being referred to the ferric salt originally present.

TABLE II.

| V, liters. | $10^3 \mu$ . |
|------------|--------------|
| 4          | 248.1        |
| 8          | 390.4        |
| 16         | 506.6        |
| 32         | 612.8        |
| 64         | 716.7        |
| 128        | 823.8        |
| 256        | 930.6        |
| 512        | 1037.5       |
| 1024       | 1141.2       |
| 2048       | 1244.0       |

The solutions remained perfectly clear throughout, and ionization appears to be more nearly complete than before. By repeating these experiments several times with fresh preparations of ferric alum, slightly different values were found for the original resistances and those after reduction. The limits for the first were 281.5 to 282.5, and for the last 125 to 127.

In the reduction of the ferric alum, ferrous sulphate, ammonium sulphate and free sulphuric acid are formed. I next prepared a solution of these substances in the proportions which would result from the reduction of the amount of ferric alum taken above. The solution contained :

|                                    | Grams. |
|------------------------------------|--------|
| Sugar .....                        | 100.0  |
| Crystallized ferrous sulphate..... | 69.5   |
| Ammonium sulphate.....             | 16.5   |
|                                    | cc.    |
| Normal sulphuric acid.....         | 250    |
| Water to make .....                | 500    |

With this solution a resistance of 125.8 ohms was found at 20.5°, which corresponds very closely to 127 ohms at 20°. Indeed, this result is much closer than one at first thought

might expect, when it is remembered that a part of the sugar suffers oxidation during the reduction of the salt. But practically the same figures were found in many subsequent trials, from which it is evident that the resistance of the sugar is not greatly changed by inversion and partial oxidation. It is probable that the products formed are but slightly dissociated. A few experiments were made to throw light on this point. A solution was prepared containing in 250 cc. 60.25 grams of ferric alum and an amount of pure dry crystallized dextrose to correspond to fifty grams of cane sugar (52.6 grams). The resistance of this at 20.5°, was found to be 279.2 ohms. The resistance of dextrose is therefore practically the same as that of cane sugar. This solution was heated to 70° through several hours, but still remained yellowish brown, and deposited finally a basic precipitate. A solution was next made containing in 250 cc. fifty grams of dextrose, fifty-five grams of ferric alum and twenty-five cc. of normal sulphuric acid. The resistance was found to be 230.5 ohms at 20.2°. A portion of the solution was heated two hours at 95°; it remained dark and deposited a slight basic precipitate. The resistance was now found to be 195.6 ohms at 20.3°, which is a relatively small change. Finally I made a solution with fifty grams of cane sugar, 60.25 grams of ferric alum and twenty-five cc. of normal sulphuric acid in 250 cc. The sugar was inverted by the acid before the alum was added, and for the mixture a resistance of 244.3 ohms at 20.2° was found. After heating to 95° through two hours, the resistance was reduced to 111 ohms at 20°, while tests showed the ferric salt to be wholly reduced. It would appear from the above that the reduction is largely due to the levulose of the inverted sugar, and this agrees with the known behavior of levulose in other reactions.

That the resistance after reduction corresponds closely to that found from mixtures of the reduction products according to the equations assumed above, was found in other cases where larger and smaller amounts of sugar were used with the given weights of the salts. This established, we have evidently a very simple means at hand for determining the speed of the reduction reaction, by determination of resistances from time to time, the results being compared with the resistances found from known mixtures.

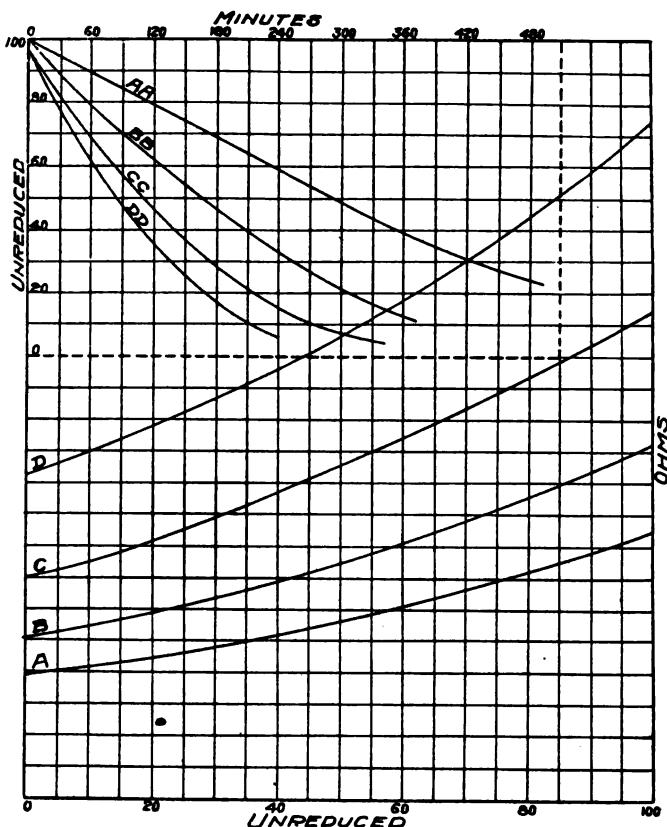
of acid, ferric and ferrous salts and ammonium sulphate. These mixtures were made to contain amounts of ferric alum, ferrous sulphate, ammonium sulphate and acid corresponding to those present at different stages in the reduction. In the following table are given the weights of the pure materials mixed, the iron salts being taken in the crystallized condition.

TABLE III.  
*For 250 cc. of Solution.*

| Sugar.<br>Grams. | Ferric<br>alum.<br>Grams. | Ferrous<br>sulphate.<br>Grams. | Ammonium<br>sulphate.<br>Grams. | Normal<br>sulphuric<br>acid.<br>cc. | Ferric<br>salt.<br>Per cent. | Resistance<br>in<br>ohms. |
|------------------|---------------------------|--------------------------------|---------------------------------|-------------------------------------|------------------------------|---------------------------|
| 50               | 60.25                     | ....                           | ....                            | ..                                  | 100                          | 282.1                     |
| 50               | 48.20                     | 6.95                           | 1.65                            | 25                                  | 80                           | 241.6                     |
| 50               | 36.15                     | 13.90                          | 3.30                            | 50                                  | 60                           | 204.6                     |
| 50               | 24.10                     | 20.85                          | 4.95                            | 75                                  | 40                           | 173.2                     |
| 50               | 12.05                     | 27.80                          | 6.60                            | 100                                 | 20                           | 148.3                     |
| 50               | ....                      | 34.75                          | 8.25                            | 125                                 | 00                           | 126.6                     |

In the last column the resistances in ohms for the several solutions are given. I have not thought it necessary to calculate the corresponding conductivities, as the direct determinations are sufficient for all comparisons to be made. By means of coordinate paper, I have plotted a curve from these values on a large scale, and from this curve the resistance of any intermediate mixture may be found with a high degree of accuracy. The form of this curve is shown in the accompanying figure at *B*. In making the above mixtures the ferric alum was dissolved in part of the water by the aid of heat; the solution was then cooled to 20°. The sugar and the other substances were then dissolved in more water, the cooled mixture was added to the ferric alum and the whole brought to 250 cc. at 20°. At this temperature the ferric alum changes very slowly, and not appreciably during the time of an experiment. The sugar in the mixtures was probably mostly in the inverted condition. Experiments with mixtures, as in the above table, were repeated several times and always practically with the same results.

The data secured in the manner described were applied to follow the speed of reduction in a solution warmed in the thermostat. I made a solution with 241 grams of ferric alum in 500 cc. at 20°, and another with 200 grams of sugar in 500 cc. These solutions were warmed to 70° and mixed. The mixture



was divided among eight flasks holding over 100 cc. each. The flasks were closed with capillary stoppers and were supported in a frame to be immersed in the thermostat and rotated. While being filled, the flasks were kept at a temperature of 66°, and this was the exact temperature of the thermostat in all experiments. The liquids mixed at 70° cooled to about 66° during the filling, and after immersion in the water the flasks remained fifteen minutes before the first one was removed for an observation; this to allow the temperature to become constant. Some preliminary experiments were carried out at a temperature of 75°, but here it was found that the reaction was completed too quickly for accurate observation. In another series of tests at 55° the time required to complete the tests was found to be too

long. Finally 66° was chosen as the temperature best suited to all the experiments contemplated.

In the table below the results obtained by testing the solutions from the eight flasks are given. The first column shows the time at which each flask was removed from the thermostat and quickly cooled. The second column shows the resistance found at 20°, while in the third column the amount of ferric salt remaining is expressed in per cent. for each test.

TABLE IV.

| Time. | Ohms. | 'Unreduced. |
|-------|-------|-------------|
| 9.00  | 281.4 | 99.5        |
| 9.30  | 262.9 | 90.5        |
| 10.00 | 240.6 | 79.3        |
| 11.00 | 207.9 | 62.5        |
| 12.00 | 182.5 | 46.8        |
| 1.00  | 163.6 | 33.0        |
| 2.00  | 149.6 | 21.6        |
| 3.00  | 140.4 | 13.5        |

The numbers in the third column are obtained by interpolation from the curve referred to above. When these numbers are plotted in the same manner, with the times in minutes (duration of heating) as abscissas, a very regular curve, shown at *BB*, is obtained. An inspection of the curve and the table is sufficient to show that the speed of the reduction decreases slowly at the start; the law of the reduction is not immediately apparent, but this will be taken up later.

It was thought best to make other tests with larger and smaller amounts of sugar, and the results of these will be given below. As preliminary, however, I determined roughly the behavior of constant amounts of ferric alum with varying amounts of sugar, and this is shown in the following table. Five solutions of 100 cc. each were made, and these were heated three hours to 75° in the thermostat.

TABLE V.

| No. | Amount of alum. | Amount of sugar. | Ratio of alum to sugar.<br>Mol. | Results.                 |
|-----|-----------------|------------------|---------------------------------|--------------------------|
| 1   | 24.1            | 4.275            | 1 : $\frac{1}{6}$               | Heavy basic precipitate. |
| 2   | 24.1            | 8.550            | 1 : 1                           | Slight precipitate.      |
| 3   | 24.1            | 17.10            | 1 : 2                           | Clear, slightly colored. |
| 4   | 24.1            | 25.65            | 1 : 3                           | Clear, dark.             |
| 5   | 24.1            | 34.20            | 1 : 4                           | Clear, dark.             |

It is evident, therefore, that the proportion of sugar in the first is much too low; in the second it is slightly low, while in the others it is sufficient.

I made next solutions of 250 cc., with the amounts of sugar and salts as shown in the following table, and found the corresponding resistances given in the last column, in ohms at 20°.

TABLE VI.

*For 250 cc. of Solution.*

| Sugar.<br>Grams. | Ferric<br>alum.<br>Grams. | Ferrous<br>sulphate.<br>Grams. | Ammonium<br>sulphate.<br>Grams. | Normal<br>sulphuric<br>acid.<br>cc. | Ferric<br>salt.<br>Per cent. | Resistance<br>in ohms. |
|------------------|---------------------------|--------------------------------|---------------------------------|-------------------------------------|------------------------------|------------------------|
| 25               | 60.25                     | ....                           | ....                            | ....                                | 100                          | 213.0                  |
| 25               | 48.20                     | 6.95                           | 1.65                            | 25                                  | 80                           | 181.0                  |
| 25               | 36.15                     | 13.90                          | 3.30                            | 50                                  | 60                           | 152.5                  |
| 25               | 24.10                     | 20.85                          | 4.95                            | 75                                  | 40                           | 130.0                  |
| 25               | 12.05                     | 27.80                          | 6.60                            | 100                                 | 20                           | 111.2                  |
| 25               | ....                      | 34.75                          | 8.25                            | 125                                 | 00                           | 96.2                   |

A curve plotted from these figures is shown at *A*. This curve was used as before to calculate the proportions of ferric and ferrous salts, in mixtures undergoing reduction, from observations of resistance.

A solution for the thermostat was prepared containing in 1000 cc. 100 grams of sugar and 241 grams of ferric alum. As in the former case, the sugar and alum were dissolved separately and made up to 500 cc., mixed and distributed in the small flasks as before. The table below gives the result of the tests, the thermostat being kept at 66°, and the first flask removed at the end of fifteen minutes.

TABLE VII.

| Time. | Ohms. | Unreduced. |
|-------|-------|------------|
| 9.00  | 213.6 | 100.0      |
| 10.30 | 190.4 | 86.0       |
| 12.00 | 165.0 | 69.5       |
| 1.00  | 151.3 | 59.0       |
| 2.00  | 138.8 | 48.5       |
| 3.00  | 129.4 | 40.0       |
| 4.00  | 121.5 | 31.6       |
| 5.00  | 115.5 | 25.5       |

The results of the last column are plotted and shown at *AA*. It will be observed that the rate of reduction is much slower here than in the former case. It was also noticed that the last

flasks removed from the thermostat were slightly turbid from partial dissociation.

Two other sets of solutions were studied. The details of the results are here given.

TABLE VIII.  
For 250 cc. of Solution.

| Sugar.<br>Grams. | Ferric<br>alum.<br>Grams. | Ferrous<br>sulphate.<br>Grams. | Ammonium<br>sulphate.<br>Grams. | Normal<br>sulphuric<br>acid.<br>cc. | Ferric<br>salt.<br>Per cent. | Resistance<br>in ohms. |
|------------------|---------------------------|--------------------------------|---------------------------------|-------------------------------------|------------------------------|------------------------|
| 75               | 60.25                     | ....                           | ...                             | ...                                 | 100                          | 386.5                  |
| 75               | 48.20                     | 6.95                           | 1.65                            | 25                                  | 80                           | 333.5                  |
| 75               | 36.15                     | 13.90                          | 3.30                            | 50                                  | 60                           | 285.0                  |
| 75               | 24.10                     | 20.85                          | 4.95                            | 75                                  | 40                           | 243.2                  |
| 75               | 12.05                     | 27.80                          | 6.60                            | 100                                 | 20                           | 206.4                  |
| 75               | ....                      | 34.75                          | 8.25                            | 125                                 | 00                           | 177.1                  |

In curve C the results of the observations are found plotted. A mixture of 300 grams of sugar and 241 grams of ferric alum was made and used in the thermostat as before. The resistance found and the amount of reduction are tabulated below.

TABLE IX.

| Time. | Ohms. | Unreduced. |
|-------|-------|------------|
| 8.30  | 379.1 | 97.4       |
| 9.30  | 304.4 | 68.5       |
| 10.15 | 264.8 | 50.5       |
| 11.00 | 237.3 | 37.0       |
| 11.45 | 214.7 | 25.0       |
| 12.30 | 199.8 | 16.0       |
| 1.15  | 191.2 | 10.0       |
| 2.00  | 184.4 | 5.5        |

The results of this test are plotted and shown in curve CC, which is very regular, without any sharp breaks.

Finally a series of concentrated solutions were made to fully test the effect of increased amounts of sugar on the speed of the reaction. It was found that 400 grams to the liter could be brought into solution with the amount of salts taken, and the table below shows the results obtained with such mixtures.

TABLE X.  
For 250 cc. of Solution.

| Sugar.<br>Grams. | Ferric<br>alum.<br>Grams. | Ferrous<br>sulphate.<br>Grams. | Ammonium<br>sulphate.<br>Grams. | Normal<br>sulphuric<br>acid.<br>cc. | Ferric<br>salt.<br>Per cent. | Resistance<br>in ohms. |
|------------------|---------------------------|--------------------------------|---------------------------------|-------------------------------------|------------------------------|------------------------|
| 100              | 60.25                     | ....                           | ..                              | ...                                 | 100                          | 538.0                  |
| 100              | 48.20                     | 6.95                           | 1.65                            | 25                                  | 80                           | 462.3                  |
| 100              | 36.15                     | 13.90                          | 3.30                            | 50                                  | 60                           | 397.5                  |
| 100              | 24.10                     | 20.85                          | 4.95                            | 75                                  | 40                           | 341.2                  |
| 100              | 12.05                     | 27.80                          | 6.60                            | 100                                 | 20                           | 296.0                  |
| 100              | ....                      | 34.75                          | 8.25                            | 125                                 | 00                           | 261.0                  |

Curve *D* was plotted from these observations.

A corresponding mixture with 400 grams of sugar and 241 grams of ferric alum was then investigated after heating in the thermostat to 66° as before. The results show a greater rapidity in the reduction of the ferric salt than was found in either of the other mixtures, as indicated in the following table.

TABLE XI.

| Time. | Ohms. | Unreduced. |
|-------|-------|------------|
| 8.45  | 530.4 | 98.0       |
| 9.00  | 490.9 | 87.5       |
| 9.30  | 428.8 | 70.0       |
| 10.00 | 381.2 | 54.5       |
| 10.45 | 332.9 | 36.5       |
| 11.35 | 296.1 | 20.0       |
| 12.20 | 279.4 | 11.0       |
| 12.45 | 273.3 | 7.0        |

The curve *DD*, plotted from the figures of the last column is, like the last one, very regular.

The question now presents itself, What is the law governing the rate of reduction of ferric salt? In all cases the amount of sugar is relatively great in proportion to that of the salt, if we take as our basis of comparison the salt and sugar which react in the well known Fehling test. But it must be noted that the oxidation here is much less complete than it is in that case, extending probably, to a small portion of the levulose formed only. Because of the uncertainty as to the exact nature of the reaction between the two substances taken, it would appear at first view that the rate of reduction can not be accurately expressed by a formula, but as the sugar is certainly in excess in some cases, I have calculated the speed of the reduction on the assumption that the iron salt alone undergoes a change in the reaction. From what was shown in one of the experiments cited above, it appears probable that the invert sugar, and not the cane sugar, is the reducing agent, and, further, that from the very beginning of the reaction, enough of this is possibly present to absorb all the oxygen furnished. It is also true that most of the invert sugar is still present at the end of the reaction. Looking upon the change, therefore, as a reaction of the first order, we have

$$\frac{dx}{dt} = K(A-x),$$

where  $A$  represents the ferric salt present at the beginning of the experiment, and  $x$  that reduced at the time,  $t$ . Therefore as  $x = 0$  for  $t = 0$ , we have :

$$K = \frac{1}{t} \text{ nat log } \frac{A}{A-x}.$$

The calculations below are made with common logarithms, as only the relative, not the actual values are considered. Table XII gives the value of  $K$  for the weakest of the above solutions, while in the three following tables the values for the other solutions are given.

TABLE XII.  
100 Grams Solution.  $A = 100$ .

| $t$ . | $x$ . | $\log \frac{A}{A-x}$ | $\frac{1}{t} \log \frac{A}{A-x}$ |
|-------|-------|----------------------|----------------------------------|
| 0     | 0     | .....                | .....                            |
| 90    | 14.0  | 0.06550              | 0.00073                          |
| 180   | 30.5  | 0.15802              | 0.00088                          |
| 240   | 41.0  | 0.22915              | 0.00095                          |
| 300   | 51.5  | 0.31426              | 0.00105                          |
| 360   | 60.0  | 0.39794              | 0.00111                          |
| 420   | 68.4  | 0.50031              | 0.00119                          |
| 480   | 74.5  | 0.59346              | 0.00124                          |

TABLE XIII.  
200 Grams Solution.  $A = 99.5$ .

|     |      |         |         |
|-----|------|---------|---------|
| 0   | 0    | .....   | .....   |
| 30  | 9.0  | 0.04117 | 0.00137 |
| 60  | 20.2 | 0.09855 | 0.00164 |
| 120 | 37.0 | 0.20194 | 0.00168 |
| 180 | 52.7 | 0.32757 | 0.00182 |
| 240 | 66.5 | 0.47931 | 0.00199 |
| 300 | 77.9 | 0.66337 | 0.00221 |
| 360 | 86.0 | 0.86745 | 0.00241 |

TABLE XIV.  
300 Grams Solution.  $A = 97.4$ .

|     |      |         |         |
|-----|------|---------|---------|
| 0   | 0    | .....   | .....   |
| 60  | 28.9 | 0.15287 | 0.00254 |
| 105 | 46.9 | 0.28527 | 0.00262 |
| 150 | 60.4 | 0.42036 | 0.00280 |
| 195 | 72.4 | 0.59162 | 0.00303 |
| 240 | 81.4 | 0.78444 | 0.00326 |
| 285 | 87.4 | 0.98856 | 0.00347 |
| 330 | 91.9 | 1.24820 | 0.00378 |

TABLE XV.  
400 Grams Solution.  $A = 98$ .

| $t.$ | $x.$ | $\log \frac{A}{A-x}$ | $\frac{1}{t} \log \frac{A}{A-x}$ |
|------|------|----------------------|----------------------------------|
| 0    | 0    | .....                | .....                            |
| 15   | 10.5 | 0.04922              | 0.00328                          |
| 45   | 28.0 | 0.14613              | 0.00325                          |
| 75   | 43.5 | 0.25483              | 0.00339                          |
| 120  | 61.5 | 0.42894              | 0.00357                          |
| 170  | 78.0 | 0.69020              | 0.00406                          |
| 215  | 87.0 | 0.94984              | 0.00442                          |
| 240  | 91.0 | 1.14623              | 0.00477                          |

A consideration of the above figures shows at once that the hypothesis regarding the nature of the reaction is not the right one, as the speed increases regularly from the beginning to the end. In other words, the speed is an accelerated one, and the cause of this acceleration may be found in the sulphuric acid liberated as the reduction advances. The acid liberated is proportional to the ferric salt reduced, and may be measured, therefore, by  $x$ .

It is evident also from the tables that the speed of the reaction varies with the amount of sugar in the solution, as it is almost four times as great with the 400 grams solution as with the 100 grams solution. In any one experiment, however, this sugar amount may be considered as remaining practically constant, and a new equation expressing the speed may now be written with two terms:

$$\frac{dx}{dt} = K(B+x)(A-x),$$

in which  $B$  represents amount of sugar.

This on integration yields :

$$Kt = \frac{1}{A+B} \log \frac{B+x}{A-x} + \text{Cons.}$$

As  $x = 0$  for  $t = 0$ , we have for the definite integral :

$$Kt = \frac{1}{A+B} \log \frac{(B+x)A}{(A-x)B}$$

Before this formula can be used for practical calculations some numerical value must be given to  $B$ . From preliminary tests referred to above, it appears that the sugar amount is prob-

ably a little low in the weakest solution and high in the strongest to be considered chemically equivalent to  $A$ . However, for simplicity in calculation, it may be assumed that  $A$  and  $B$  are equal, when our formula becomes :

$$K = \frac{1}{2At} \log \frac{A+x}{A-x}$$

On this assumption the tables below have been calculated. For the 100 grams sugar solution the value of  $K$  for  $B = 0.75 A$  is added in the last column, and for the 400 grams solution the value for  $B = 2A$ .

TABLE XVI.  
100 Grams Solution.  $A = 100$ .

| $t$   | $x$  | $\frac{1}{2A} \log \frac{A+x}{A-x}$ | $\frac{1}{2At} \log \frac{A+x}{A-x}$ | $\frac{1}{t(A+B)} \log \frac{A(B+x)}{B(A-x)}$ |
|-------|------|-------------------------------------|--------------------------------------|---|
| 0     | 0    | .....                               | .....                                | .....   |
| 90    | 14.0 | 0.000612                            | 0.00000679                           | 0.00000888                                    |
| 180   | 30.5 | 0.001385                            | 0.00000760                           | 0.00000969                                    |
| 240   | 41.0 | 0.001892                            | 0.00000788                           | 0.00000996                                    |
| 300   | 51.5 | 0.002473                            | 0.00000824                           | 0.00001031                                    |
| 360   | 60.0 | 0.003010                            | 0.00000856                           | 0.00001037                                    |
| 420   | 68.4 | 0.002632                            | 0.00000865                           | 0.00001064                                    |
| 480   | 74.5 | 0.004176                            | 0.00000820                           | 0.00001063                                    |
| <hr/> |      |                                     |                                      |   |
|       |      |                                     | 0.00000802                           |   |

TABLE XVII.  
200 Grams Solution.  $A = 99.5$ .

|       |      |          |            |
|-------|------|----------|------------|
| 0     | 0    | .....    | .....      |
| 30    | 9.0  | 0.000395 | 0.00001319 |
| 60    | 20.2 | 0.000896 | 0.00001497 |
| 120   | 37.0 | 0.001704 | 0.00001420 |
| 180   | 52.7 | 0.002573 | 0.00001430 |
| 240   | 66.4 | 0.003525 | 0.00001469 |
| 300   | 77.9 | 0.004595 | 0.00001532 |
| 360   | 86.0 | 0.005718 | 0.00001586 |
| <hr/> |      |          |            |
|       |      |          | 0.00001465 |

TABLE XVIII.  
300 Grams Solution.  $A = 97.4$ .

|       |      |          |           |
|-------|------|----------|-----------|
| 0     | 0    | .....    | .....     |
| 60    | 28.9 | 0.001364 | 0.0000227 |
| 105   | 46.9 | 0.002340 | 0.0000223 |
| 150   | 60.4 | 0.003233 | 0.0000215 |
| 195   | 72.4 | 0.004271 | 0.0000218 |
| 240   | 81.4 | 0.005381 | 0.0000224 |
| 285   | 87.4 | 0.006502 | 0.0000228 |
| 330   | 91.9 | 0.007888 | 0.0000239 |
| <hr/> |      |          |           |
|       |      |          | 0.0000225 |

TABLE XIX.  
100 Grams Solution.  $A = 98$ .

| $t.$ | $x.$ | $\frac{1}{2A} \log \frac{A+x}{A-x}$ | $\frac{1}{2At} \log \frac{A+x}{A-x}$ | $\frac{1}{t(A+B)} \log \frac{A(B+x)}{B(A-x)}$ |
|------|------|-------------------------------------|--------------------------------------|---|
| 0    | 0    | .....                               | .....                                | .....   |
| 15   | 10.5 | 0.000477                            | 0.0000317                            | 0.0000163                                     |
| 45   | 28.0 | 0.001302                            | 0.0000289                            | 0.0000154                                     |
| 75   | 43.5 | 0.002114                            | 0.0000282                            | 0.0000155                                     |
| 120  | 61.5 | 0.003267                            | 0.0000272                            | 0.0000155                                     |
| 170  | 78.0 | 0.004819                            | 0.0000283                            | 0.0000167                                     |
| 215  | 87.0 | 0.006254                            | 0.0000291                            | 0.0000175                                     |
| 240  | 91.0 | 0.007303                            | 0.0000304                            | 0.0000185                                     |
|      |      |                                     | 0.0000291                            |   |

It appears from the above tables that the constants calculated from the simple formula, with  $A = B$ , are somewhat more regular than those from the other. In the first experiment, with the 100 grams solution, the reaction was not complete, and the results are at best unsatisfactory. But in the others these mean values for the speed

$$\begin{aligned} &0.0000146 \\ &0.0000225 \\ &0.0000291 \end{aligned}$$

stand to each other almost exactly in the relation 2 : 3 : 4, showing the close relation of speed to dissolved sugar. In each series the values for  $K$  are as uniform as could be expected, and show that the formula chosen represents the reaction very well.

CHICAGO, JULY 3, 1897.

## THE EXACT ESTIMATION OF TOTAL CARBOHYDRATES IN ACID HYDROLYZED STARCH PRODUCTS.

BY GEO. W. ROLFE AND W. A. FAXON.

Received June 11, 1897.

THE determination of the exact amount of carbohydrates present in solutions of commercial glucose has always been conjectural, since the evaporation method, the only available means of estimation, has always caused in the residue an intermediate amount of decomposition, usually attributed to oxidation or the destructive effect of high temperature. Since, however, in acid hydrolyzed starch products, it seems certain that the component carbohydrates preserve their individuality

throughout the combinations which they may make with each other, at least so far as to have constant optical and chemical properties, as well as a constant influence on the specific gravity per unit weight of each present in solution, it is quite possible to determine the *proportional amount* of each constituent by the use of one arbitrary specific factor throughout the calculation. This has been explained in detail in several publications of O'Sullivan, Brown, Heron, Morris, and others. It is also well known that the factor used is that representing the increase in specific gravity caused by one gram of cane sugar in 100 cc. of solution.

It follows that if the specific gravity influences of the isolated carbohydrates were known it would be quite possible to predict the specific gravity factor of any hydrolyzed starch product. A year ago an attempt was made by one of us to predict these factors of the hydrolyzed starch products for all rotation between the limits of possible specific rotatory powers for the factor 386. A provisional curve was plotted from the following formula :

$$\Sigma = m\Sigma_m + g\Sigma_g + d\Sigma_d.$$

$\Sigma$  being the specific gravity factor of the hydrolyzed starch product identified by its specific rotatory power ;  $m$ ,  $g$ , and  $d$ , the respective percentages of maltose, dextrose, and dextrin present ; and  $\Sigma_m$ ,  $\Sigma_g$ ,  $\Sigma_d$ , their corresponding specific gravity factors.

We considered this curve a provisional one, as we were obliged to approximate the factor for dextrin from the imperfect data of O'Sullivan, Salomon, and others, taking 0.00400 as the most probable value. The factors for dextrose and maltose were those of Salomon<sup>1</sup> for ten per cent. solutions, 0.00381 and 0.00390, respectively. We found that the plotted values of the calculated factors, where the specific rotatory powers were expressed as abscissae, formed a straight line joining the plots corresponding to the factors taken for pure dextrin and dextrose at the corresponding rotation of 195° and 53.5°.

Having defined approximate theoretical values we have sought to confirm them by actual determinations of the total solids present in a number of representative solutions prepared as previously described.<sup>2</sup>

<sup>1</sup> *J. prakt. Chem.*, 2, 28.

<sup>2</sup> This Journal, 18, 871-872.

Much ingenious apparatus<sup>1</sup> has been devised for overcoming the decomposition in drying already referred to. The principles of one class is the introduction of a presumably inert atmosphere, such as coal gas or hydrogen. Another class uses a vacuum, which mitigates at the same time oxidation and influence of high temperature.

Apparently, experience places so little confidence in the advantages of any of these multifarious appliances, at least in the case of sugars, that the ordinary method of drying at about 100° till the continual loss does not exceed a given rate per hour, is that usually recommended. We therefore at first dried ten cc. each of solutions of hydrolyzed starch products on paper rolls at 105°-110° C.,<sup>2</sup> the rolls being placed in weighing beakers, and dried to practically constant weight in an oven kept at the given temperature. The results obtained were discordant, and in general lower than those of our provisional curve.

A second series of determinations were made by drying paper rolls, prepared in a similar way, in a vacuum pan, the temperature being about 40°. In breaking the vacuum, air was passed through sulphuric acid and made to enter at the bottom of the pan to avoid the descent of moist vapors. Drying by this method was exceedingly tedious, and the values obtained are much lower than given by our assumed curve, besides being discordant. They indicate the need of more heat in drying.

At this point in our work we received the important paper by Brown, Morris, and Millar,<sup>3</sup> giving the details of an elaborate investigation of the primary carbohydrates and of the products of diastase hydrolysis. In the latter the actual values were successfully predicted by a method similar to ours, but by a somewhat more exact formula, as it took into consideration variations in the factors due to those of concentration. These investigators used the drying apparatus designed by Lobray de Bryn and Von Laent<sup>4</sup> for the drying of maltose. This apparatus had worked so successfully for diastase converted solutions that we at once adopted a modification of it for our next essay. Several pieces of apparatus of the type described below (Fig. 1) were

<sup>1</sup> Wiley's Principles and Practice of Agricultural Analysis, Vol. 3; see also recent bulletin by the U. S. Department of Agriculture.

<sup>2</sup> Rolfe and Defren: this Journal, 18, 872.

<sup>3</sup> J. Chem. Soc., Jan., 1897.

<sup>4</sup> Rec. Trav. Chim., 1894, 13, 218.

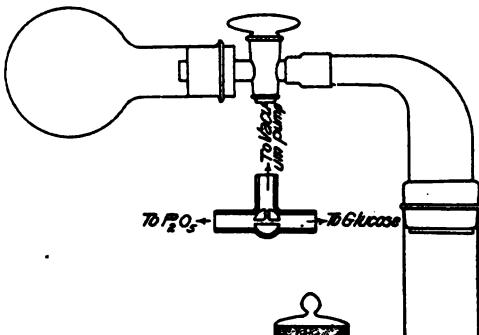


FIG. I.—APPARATUS FOR DRYING SUGARS AND GLUCOSE SYRUPS.

improvised from the stock of material available. Our apparatus is arranged so that the greater bulk of the water can be first removed without coming in contact with the phosphorus pentoxide. This avoids previous evaporation on a water-bath. The tared weighing beaker containing the solution to be evaporated is slipped on the end of the adapter, an air-tight joint being made with "bill-tie" tubing. By the three-way stop-cock, communication can be had with the vacuum pump and with a 250 cc. flask containing phosphorus pentoxide, or either can be shut off.

The method of drying is as follows: The cock is opened to the pump only, and the air exhausted to 680–690 mm. The beaker is lowered into an oil-bath and heated to about 100° till most of the water is evaporated. Communication is then made with the pentoxide flask, and the mass dried to constant weight at about 120°. For convenience, the vapor from the various pieces of apparatus were passed through a four-liter vacuum pan. This large receiver produced an almost instantaneous exhaustion when a stop-cock was opened. Complete drying usually required from eighteen to twenty-four hours. The slowness of our drying apparatus was possibly due to the contracted opening through the stop-cock, which may have prevented free circulation of vapors over the pentoxide. This drawback was the result of the necessary improvising of our apparatus from stock at hand.

The results obtained are tabulated in the following table, and

also plotted in Fig. 2. As will be seen they form a straight line

TABLE.

| No. | Time<br>drying.<br>Hours. | Vol. of<br>solution.<br>cc. | $d_{15.5}$ . | $\alpha_{D_{386}}$ | Weight of<br>residue. | Factor<br>obtained. | Factor<br>calculated. |
|-----|---------------------------|-----------------------------|--------------|--------------------|-----------------------|---------------------|-----------------------|
| 1   | 18                        | 10                          | 1.02835      | 164.2              | 0.7104                | 0.003992            | 0.003980              |
| 2   | 18                        | 10                          | 1.03134      | 160.0              | 0.7833                | 0.003999            | 0.003974              |
| 3   | 24                        | 10                          | 1.03657      | 144.8              | 0.9223                | 0.003965            | 0.003954              |
| 4   | 18                        | 10                          | 1.03364      | 141.8              | 0.8509                | 0.003954            | 0.003950              |
| 5   | 24                        | 10                          | 1.04212      | 138.7              | 1.0644                | 0.003957            | 0.003946              |
| 6   | 18                        | 10                          | 1.03650      | 136.1              | 0.9222                | 0.003953            | 0.003942              |
| 8   | 18                        | 10                          | 1.03701      | 128.0              | 0.9376                | 0.003943            | 0.003931              |
| 9   | 24                        | 10                          | 1.03701      | 128.0              | 0.9417                | 0.003930            | 0.003931              |
| 11  | 18                        | 10                          | 1.03841      | 115.7              | 0.9781                | 0.003927            | 0.003918              |
| 12  | 18                        | 10                          | 1.03704      | 111.7              | 0.9454                | 0.003918            | 0.003911              |
| 13  | 18                        | 10                          | 1.03704      | 111.7              | 0.9465                | 0.003914            | 0.003911              |
| 15  | 24                        | 10                          | 1.03843      | 104.7              | 0.9827                | 0.003910            | 0.003901              |
| 16  | 18                        | 10                          | 1.03545      | 90.5               | 0.9127                | 0.003885            | 0.003883              |
| 17  | 18                        | 10                          | 1.03594      | 81.3               | 0.9282                | 0.003883            | 0.003871              |
| 18  | 18                        | 10                          | 1.03549      | 73.4               | 0.9162                | 0.003870            | 0.003860              |
| 19  | 18                        | 10                          | 1.03881      | 70.5               | 1.0081                | 0.003850            | 0.003856              |

(The omitted numbers are those of samples which were lost by breakage, or scorching due to loss of vacuum.)

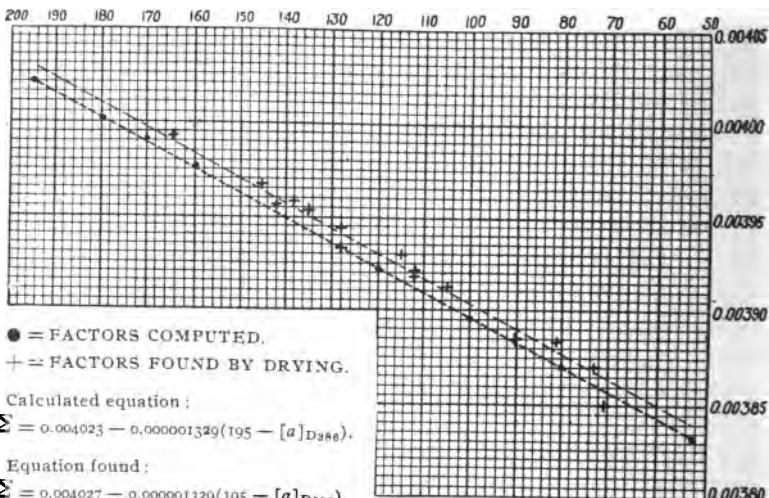


FIG. 2.—SPECIFIC GRAVITY FACTORS FOR APPROXIMATELY TEN PER CENT. SOLUTIONS OF HYDROLYZED STARCH PRODUCTS.

which is very slightly higher than the line calculated by using the revised carbohydrate value of Brown, Morris, and Millar.

The variation is very slight, as the plot is drawn on a scale by which one division represents about 0.06 per cent. of the values obtained. The two equations obtained are more nearly concordant when we take into consideration that the average of the specific gravities of the samples is about 1.0360. This would raise the calculated value 0.000003 on the scale, or a little more than one half of a division. We, therefore, have adopted as the most probable values what happens to be the mean. Our conclusion, then, is that within the concentrations expressed by the specific gravity factors, 1.035 and 1.045, we can calculate the absolute specific gravity influence of any acid hydrolyzed starch solution by the equation,  $\Sigma = 0.004023 - 0.000001329(195 - [\alpha]_D)$ , when the specific rotatory power (obtained by the factor 0.00386) is known. These values within the limits of concentration given are correct to less than two-tenths per cent. of their values. For commercial glucoses, the factor 0.00393, taken as a constant, is sufficiently exact for most determinations.

While this equation will now enable us to determine the exact amount of carbohydrate in solution when the specific gravity has been previously corrected for the influence of other dissolved material, the simpler computation based on the factor 0.00386 will doubtless continue in use as more convenient for those calculations where proportion of carbohydrates is alone desired.

We have also under investigation the action of heat on commercial glucoses when samples are boiled down to candies, as well as the study of certain disturbing influences on the determination of cupric reducing powers of glucoses. The results are not yet complete enough for publication.

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#### A FURTHER COMMUNICATION ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMO- NIUM PHOSPHOMOLYBDATE PRECIPI- TATE WITH STANDARD ALKALI.

By B. W. KILGORE.

Received June 17, 1897.

DURING the past four years the writer has done a great deal of work on this method,<sup>1</sup> and the results obtained in this laboratory for the past two years, at least, by five analysts,

<sup>1</sup> Bul. 43 and 47, pp. 68-104 and 62-83, Chem. Div., U. S. Department of Agriculture; Bul. 119, North Carolina Experiment Station: and this Journal, 16 and 17, Nos. 11 and 12.

warrant us in considering it thoroughly accurate and reliable. More recently the method has been extensively and successfully employed in experiment station and other laboratories. Some chemists, however, have not been able to get uniformly good results with it. These appear to be mostly those who have worked the method but little; while the difficulty with others seems to be due to a misunderstanding as to how the method should be carried out.

At the last meeting of the Association of Official Agricultural Chemists, two main objections were brought against its adoption as an official method at that time. One was that it had not been tried upon a sufficient variety of fertilizers and fertilizer materials used in the trade to show that it would give as good results on all of them as it had upon those it had been worked upon, when in the hands of those who had worked the method to any extent.

The other objection was that brought out in the paper<sup>1</sup> of Mr. T. S. Gladding. Mr. Gladding had made twenty-two comparative tests of the volumetric method with the official gravimetric method and his gravimetric method on a microcosmic salt and various fertilizers with closely agreeing results in all cases. He then turned over a set of precipitates to an assistant to filter and wash free of acids, according to the method. It was found that the precipitates could not be freed from acid; and upon closer examination it was observed that the water was dissolving the precipitate.

The experiments, the results of which follow in the table, were planned to throw light upon, and if possible to settle, these two questions.

<sup>1</sup> Bul. 49, Chem. Div., U. S. Department of Agriculture, p. 75.

**COMPARATIVE PHOSPHORIC ACID RESULTS ON VARIOUS FERTILIZER MATERIALS BY GRAVIMETRIC AND VOLUMETRIC METHODS.**

| Materials.                             | Gravimetric method. |                       | Washed with<br>Cc. water. | Washed with<br>three per cent.<br>ammonium ni-<br>trate solution. | Washed with<br>three per cent.<br>potassium ni-<br>trate solution. | Amount of so-<br>lution correc-<br>ted for loss of<br>substance used in volu-<br>metric method. | Grams. |
|--|---------------------|-----------------------|---------------------------|---|--|---|--------|
|  | Per cent.           | Volumetric<br>method. |                           |   |  |   |        |
| 1. Cottonseed meal....                 | 2.97                | 2.97                  | 200                       | ...   | ...  | ...   | 0.2    |
|  | ...                 | 2.93                  | 500                       | ...   | ...  | ...   | 0.2    |
|  | 2.96                | 2.91                  | 500                       | ...   | ...  | ...   | 0.2    |
| 2. Tankage .....                       | 11.62               | 11.68                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | 11.67               | 11.58                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 11.60                 | ...                       | 200   | ...  | ...   | 0.2    |
| 3. North Carolina phos-<br>phate ..... | 18.27               | 18.20                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | 18.27               | 18.20                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 18.18                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | ....                | 17.88                 | ...                       | 500   | ...  | ...   | 0.2    |
| 4. South Carolina phos-<br>phate ..... | 27.98               | 28.06                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | 27.98               | 28.09                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 28.04                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | ....                | 27.74                 | ...                       | 500   | ...  | ...   | 0.2    |
| 5. Pennsylvania phos-<br>phate .....   | 18.59               | 18.59                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | 18.58               | 18.56                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 18.56                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | ....                | 18.34                 | ...                       | 500   | ...  | ...   | 0.2    |
| 6. Thomas slag (Amer-<br>ican).....    | a16.38              | 16.05                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | a16.43              | 16.00                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | b16.14              | 15.98                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | c16.04              | 15.75                 | ...                       | 500   | ...  | ...   | 0.2    |
| 7. Thomas slag (Euro-<br>pean).....    | a18.15              | 17.98                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | a18.08              | 17.97                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | c17.90              | 17.88                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | ....                | 17.73                 | ...                       | 500   | ...  | ...   | 0.2    |
| 8. Bone meal.....                      | 22.14               | 22.10                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | 22.02               | 22.08                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 22.00                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | ....                | 21.95                 | ...                       | 500   | ...  | ...   | 0.2    |
| 9. Acid phosphate ....                 | 17.44               | 17.56                 | 200                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 17.51                 | 500                       | ...   | ...  | ...   | 0.2    |
|  | ....                | 17.51                 | ...                       | 200   | ...  | ...   | 0.2    |
|  | ....                | 17.30                 | ...                       | 500   | ...  | ...   | 0.2    |

| Materials.                                   | Grimmett<br>method. | Volumetric<br>method. | Washed with<br>water. | Washed with<br>three per cent.<br>ammonium ni-<br>trate solution. | Washed with<br>three per cent.<br>potassium ni-<br>trate solution. | Amount of so-<br>lution corres-<br>ponding to<br>g'm's sub'snce<br>used in volu-<br>metric method. |
|--|---------------------|-----------------------|-----------------------|---|--|--|
| 10. Mixed fertilizer .....                   | 10.23               | 10.40                 | 200                   | ...   | ...  | 0.2  |
|  | 10.25               | 10.35                 | 500                   | ...   | ...  | 0.2  |
| 11. Tennessee phosphate<br>(low grade).....  | 23.08               | 23.11                 | 200                   | ...   | ...  | 0.2  |
|  | ....                | 23.11                 | 500                   | ...   | ...  | 0.2  |
| 12. Tennessee phosphate<br>(high grade)..... | 35.07               | 35.00                 | 200                   | ...   | ...  | 0.1  |
|  | 34.85               | 35.00                 | 500                   | ...   | ...  | 0.1  |
| 13. Aluminum phosphate                       | 46.91               | 47.10                 | 200                   | ...   | ...  | 0.1  |
|  | 46.82               | 47.20                 | 500                   | ...   | ...  | 0.1  |
|  | 47.00               | ....                  | ...                   | ...   | ...  | .  |
| 14. Florida phosphate..                      | 37.74               | 37.80                 | 200                   | ...   | ...  | 0.1  |
|  | 37.62               | 37.78                 | 500                   | ...   | ...  | 0.1  |
| 15. Sodium phosphate..                       | 19.97               | 19.96                 | 200                   | ...   | ...  | 0.2  |
|  | 20.07               | 19.90                 | 500                   | ...   | ...  | 0.2  |
|  | 20.03               | 19.76                 | ...                   | ...   | 200  | 0.2  |
|  | 19.97               | 18.68                 | ...                   | ...   | 500  | 0.2  |
|  | 19.82               | 19.90                 | ...                   | 200   | ...  | 0.2  |
|  | ....                | 19.82                 | ...                   | 500   | ...  | 0.2  |

Sample No. 6, American Thomas slag, contained a very large amount of iron, while No. 7, European slag, contained considerable iron. "a" were precipitated only once with molybdic solution, and the "white" precipitates were contaminated with iron. "b c" were precipitated twice with molybdic solution to get rid of iron." The "white" precipitates giving results "c c" were free from iron, but "b" still contained a very small amount.

*Note.*—The solutions used in this work were the same as those given in the description of the method in Bul. 46, Div. Chem., U. S. Department of Agriculture, p. 13.

With reference to the variety of materials, an examination of the publications referred to at bottom of page 703, under reference (1), will show that the method has already been worked upon quite a variety of fertilizer materials and mixed goods, which with the materials investigated in this paper, appears to include nearly all, if not all, the sources of phosphoric acid in the fertilizer trade. Besides these, the large number of results presented to the Association last year by Mr. John P. Street, and

published in the Annual Report of the New Jersey Station,<sup>1</sup> shows that the method gives good results on mixed goods. Mr. Street says: "The materials analyzed included 276 samples of complete fertilizers, of varying composition and origin; and are believed to fairly represent the average goods on the market at the present time. The results secured were extremely satisfactory, the average results by the volumetric method being 10.72 per cent. against 10.70 per. cent. by the official method. Of these results, 150 were higher by the volumetric, 113 lower, and thirteen identical with the official method; the greatest variation was 0.16 per cent., and 114 samples varied less than 0.05 per cent."

The results obtained by both the gravimetric and volumetric methods on the samples reported upon in this paper show good agreement, except those on samples 6 and 7, American and European manufactured Thomas slags. The American slag contained a very large amount of iron, and the European one quite a considerable quantity. When the yellow precipitates from these samples were dissolved on the filter with dilute ammonia water considerable iron remained on the filter. The results marked "a" in the table were secured by carrying these through according to the usual custom without reprecipitating to get rid of iron. These "a" results are about 0.40 per cent. higher than the corresponding volumetric ones on the American slag, and considerably higher on the European one. The "white" precipitates giving these high results were seen by color and shown by chemical test to contain iron. A second set of determinations was then made, using the same solutions from which the above results were obtained and precipitating twice with molybdic solution to get rid of iron, when results "c, c and b" were secured. These results show close agreement with the volumetric ones. Result "b" still contained a small amount of iron.

It appears then that the volumetric method has not only given as good results on all the samples here worked, including the *very high percentages*, as the gravimetric method, but on the samples containing large amounts of iron the results were better. I might state in this connection that we have found the

<sup>1</sup> 17th Annual Report, p. 118.

volumetric method to give very satisfactory results in estimating the phosphoric acid in soils, where a large amount of iron is usually present.<sup>1</sup>

Now as to Mr. Gladding's point of telling when the precipitate has been washed sufficiently. It might be stated here also that others have had difficulty at this point and the statement in the method as published in Bulletin 46, Chemical Division, United States Department of Agriculture, p. 14, to wash the precipitate "till no longer acid" is responsible to some extent at least for this trouble.

It is well known that ammonium phosphomolybdate is slightly soluble in water and is an acid salt; and it would therefore be impossible to get a filtrate from washing with water that would be strictly neutral to very delicate indicators, like phenol phthalein. It will be found, however, that when the filtrate is allowed to drop from the neck of the funnel upon delicate litmus paper, that the wash water will be neutral to litmus after 100 to 200 cc. water has passed through. The work here reported and that previously done by us,<sup>2</sup> together with the work of Street,<sup>3</sup> McDonnell, and others, shows that 150 to 250 cc. water, and often less, has been sufficient in all cases to free the precipitates of acid. But as stated by the writer in a previous paper on washing the yellow precipitate, "there is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove the nitric acid. It is in this after washing, when all the salts have been removed from the precipitate and as much as 600 to 700 cc. of water has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 cc. water."<sup>4</sup> Perhaps this will explain the difficulty which occurred in Mr. Gladding's laboratory, in that more water was used for washing than was necessary. When these large quantities of water are used the precipitate not only gets through the filter and settles out in

<sup>1</sup> Bul. 47, Chem. Div., U. S. Department of Agriculture, p. 82.

<sup>2</sup> Bul. 47, Chem. Div., U. S. Department of Agriculture, p. 62.

<sup>3</sup> Seventh Annual Report, New Jersey Station, p. 118.

<sup>4</sup> This Journal, 17, 958.

the filtrate but it dissolves far more readily than when smaller amounts of water are used for washing.

In the light of the experience of the past three years, however, it does not now seem to be necessary to wash with more than 150 to 200 cc. of water, and the smaller of these is not much more, if any, than is used in washing the yellow salt in the gravimetric method.

In the results which precede in the table, I have made an additional test of the washing question by using 200 cc. and 500 cc. of water and the wash solutions, and making the determinations side by side and from the same solutions. The gravimetric results used for comparison were obtained on the same solutions as the volumetric ones. The results show that 200 cc. of water, even with these *very high percentages*, was sufficient in all cases, and that 500 cc. only lowered the results slightly when at all. Wheh 200 cc. of three per cent. ammonium and potassium nitrate solutions were used for washing the results were practically the same as those obtained when the two quantities of water were used, but when they were increased to 500 cc. the results, greatly to my surprise, were much lower. The results were so much of a surprise that quite a number of them were repeated, and while they were not uniform in all cases, they were always low. We had hoped to be able to wash with a very large volume of ammonium nitrate solution without appreciably dissolving the precipitate or causing it to run through the filter. The filtrates from these 500 cc. ammonium and potassium nitrate washes were perfectly clear, but on evaporation the ammonium phosphomolybdate was found to be in solution.

In these determinations three-inch Hirsch funnels, with disks of filter paper covering the bottoms, and right strong suction, were used in filtering. The filtrates were not tested, but other determinations on the same sample by using ordinary funnel and filter paper without pressure showed them to be free of acid, after washing with 150 to 200cc. of water. These results agreed well with those obtained with the pump. All the precipitates were washed twice by decantation with dilute nitric acid and once with potassium or ammonium nitrate solution before washing with water.

In view of the results with potassium and ammonium nitrate

solutions it is suggested that one washing by decantation with water take the place of washing with potassium nitrate, following the washing with dilute nitric.

A word may not be out of place here in regard to the titration and end reaction. The greater the amount of yellow precipitate present the more slowly does the phenolphthalein color disappear, but up to twenty per cent. or more, when two-tenths gram of substance is used, the end reaction is quite sharp. For percentages much above twenty I consider one-tenth gram substance better to use, when the end reaction will be found sharp for any percentages one will be called upon to work. To summarize: For percentages below five use four-tenths gram substances (or about); for percentages between five and twenty use two-tenths gram, and above twenty use one-tenth gram.

It will also be found that by adding the indicator after the precipitate has been dissolved in the alkali, that the molybdenum colorations which sometimes interfere with the end reaction will be avoided. This observation was made by Street in his work previously referred to, and my observations corroborate it. Of the results presented in the table, the gravimetric determinations were made by Messrs. W. M. Allen, H. K. Miller, and myself; and the volumetric ones by myself.

The volumetric method was somewhat modified at the last meeting of the Association of Agricultural Chemists, and in such a way as to get around the difficulty of excessive washing spoken of in this paper. I repeat here the method in the form it was recommended that it should be tested in the work of this year:

Dissolve two grams substance in nitric and hydrochloric acids, incinerating beforehand to destroy organic matter if necessary, and make up to volume of 200 cc. For percentages below five use forty cc. of solution, for percentages between five and twenty use twenty cc. (and for percentages above twenty use ten cc.); add five to ten cc. concentrated nitric acid, nearly neutralize with ammonia, heat in the water-bath at 60°-65° C., add fifty cc. freshly filtered molybdic solution for each one-tenth gram phosphorus pentoxide present, and digest in water-bath for ten to fifteen minutes.

Decant the clear liquid on the filter as quickly as possible,

using Hirsch funnel with suction or ordinary funnel and filter paper with or without pressure; wash the precipitate by decantation twice with sixty per cent. nitric acid solution, using about fifty cc. of the solution each time, agitating thoroughly, and allowing the precipitate to completely settle, once with the same amount of three per cent. ammonium or potassium nitrate solution,<sup>1</sup> transfer it to the filter, and wash it five or six times with water, using 150 to 250 cc.<sup>2</sup> Now wash the filter and contents back into the beaker, add excess of standard alkali, and then a few drops of phenolphthalein, and titrate back with standard nitric acid.

### THE ACTION OF NITRIC ACID UPON ALUMINUM AND THE FORMATION OF ALUMINUM NITRATE.

BY THOMAS B. STILLMAN.

Received July 17, 1897.

**T**HE bibliography of aluminum, in reference to the action of nitric acid upon the metal, is well worthy of investigation.

The statements are so conflicting, even in the recent literature bearing upon this subject, that direct experimentation was required to demonstrate the solubility of aluminum in nitric acid.

Wöhler<sup>3</sup> states: "Aluminium is not attacked by  $HNO_3 + Aq$  even when concentrated and boiling."

Deville<sup>4</sup> gives as the result of his experiments that aluminum is not attacked by boiling nitric acid, dilute or concentrated.

Richards<sup>5</sup> refers to the statement of Deville, but also adds: "In boiling acid solution takes place, but with such slowness that I had to give up this mode of dissolving the metal in my analysis." "By cooling the solution all action ceases."

Buff and Heeren<sup>6</sup> coincide with Deville, "Aluminium wird weder von verd. noch konz.  $HNO_3$ , angegriffen."

Montemartin,<sup>7</sup> "Aluminium is slowly soluble in 27 per cent.

<sup>1</sup> It is suggested that water be used for this washing by decantation instead of the nitrate solution.

<sup>2</sup> In our experience 200 cc. of water is sufficient.

<sup>3</sup> Pogg. Ann., 2, 223.

<sup>4</sup> A Dictionary of Chemical Solubilities, by Comey, 1896.

<sup>5</sup> Compt. Rend., 38, 279.

<sup>6</sup> Aluminium, its Properties, Metallurgy and Alloys, by J. W. Richards, 1890.

<sup>7</sup> Handbuch der anorganische Chemie, Dammer, 2, 86, 1894.

<sup>8</sup> Gazz. Chim. Ital., 22, 397.

$\text{HNO}_3 + \text{Aq.}$ , 100 cc.  $\text{HNO}_3 + \text{Aq.}$  requiring 2 months to dissolve 2 grams of aluminium.”<sup>1</sup>

M. M. Pattison Muir<sup>2</sup> states, in relation to the chemical properties of aluminum: “It is scarcely attacked by  $\text{HNO}_3 + \text{Aq.}$ ”

Weeren,<sup>3</sup> “Aluminium is soluble in  $\text{HNO}_3 + \text{Aq.}$  *in vacuo*.”

Storer’s Dictionary of Solubilities of Chemical substances, page 28, gives the one reference only regarding the action of nitric acid upon aluminum, *viz.*, “unacted upon by nitric acid, either concentrated or dilute, at ordinary temperatures, but is slowly dissolved therein on boiling.”

N. Menschutkin,<sup>4</sup> “Nitric acid has only a slight action upon aluminium, the layers of nitric oxide formed protecting the metal from further attack.”

Ira Remsen,<sup>5</sup> “At ordinary temperatures nitric and sulphuric acids do not act upon aluminium; at higher temperatures, however, action takes place.”

Birnbaum,<sup>6</sup> Concentrated and dilute nitric acid, either cold or warm, are without action upon aluminum. (“Concentrirt und verdünnte Salpetersäure sind in der Kälte und Wärme ohne Wirkung auf Aluminium.”)

W. Borchers,<sup>7</sup> Nitric acid is almost without action upon aluminium. (“Salpetersäure ist fast ganz unwirksam auf Aluminium.”)

Ferdinand Fischer,<sup>8</sup> “Nitric acid and sulphuric acid scarcely affects aluminium.”

J. Arthur Phillips,<sup>9</sup> “Aluminium is not attacked by cold nitric acid, and only slowly on boiling.”

Ad. Wurtz,<sup>10</sup> “Nitric acid, dilute or concentrated, has no effect upon aluminium at ordinary temperatures. On boiling, however, solution of the metal is effected with extreme slowness.”

<sup>1</sup> A Dictionary of Chemical Solubilities, by Comey, 3.

<sup>2</sup> Watt’s Dictionary of Chemistry, 1, 142, (latest edition).

<sup>3</sup> Ber. d. chem. Ges., 24, 1798.

<sup>4</sup> Analytical Chemistry, by N. Menschutkin, London, 1895, p. 64.

<sup>5</sup> Inorganic Chemistry, by Ira Remsen, N. Y., 1895, p. 452.

<sup>6</sup> Handwörterbuch der Chemie, Fehling, 1, 339.

<sup>7</sup> Lexicon der gesamten Technik, Leugler, Leipzig, 1896, 1, 262.

<sup>8</sup> Manual of Chemical Technology, (Wagner), 13th German edition as remodelled by Dr. Ferdinand Fischer, p. 223.

<sup>9</sup> Elements of Metallurgy, by J. Arthur Phillips and H. Bauermann, 528.

<sup>10</sup> Dictionnaire de Chemie, 1, 167.

Alfred E. Hunt, John W. Langley, Charles M. Hall,<sup>1</sup> "Aluminium is unaffected by either concentrated sulphuric or nitric acids."

*Encyclopedia Britannica*, 1, 647, states: "Aluminium is not attacked by nitric acid, even when the acid is concentrated,"

Charles M. Hall,<sup>2</sup> "Sulphuric and nitric acids act upon aluminium with extreme slowness, not dissolving it appreciably after several days' exposure to their action."

Henry Roscoe,<sup>3</sup> Sulphuric and nitric acids, both dilute and concentrated, have no effect upon aluminium."

Hanford Henderson,<sup>4</sup> "Aluminium is almost untouched by nitric and sulphuric acids."

G. A. Leroy,<sup>5</sup> Sulphuric and nitric acids act immediately upon aluminium. "(Schwefelsäure und salpetersäure grießen das aluminium schnell an.)"

R. L. Packard<sup>6</sup> gives a résumé of the experiments of LeRoy as follows: "LeRoy used aluminium foil having the composition of 98.28 per cent. to 99.60 per cent. aluminium; 1.60 per cent. to 0.30 per cent. iron; 0.25 per cent. to 0.10 per cent. silicon.

The foil was polished, freed from fat with caustic soda, washed with alcohol, dried in the air-bath, cut up, weighed and introduced into the acids.

| Temperature.  | Aluminum dissolved in grams per sq. meter in 12 hours. |
|---|--|
| Pure HNO <sub>3</sub> , sp. gr. 1.383..... 15°-20° C. | 17.0 grams.  |
| Common HNO <sub>3</sub> , sp. gr. 1.332 15°-20° C.    | 16.3 grams.  |
| Pure HNO <sub>3</sub> , sp. gr. 1.382..... 100° C.    | Violent action.  |

According to these results, almost pure aluminum, 99.5 per cent., is attacked even in the cold by nitric acid.

Very elaborate experiments were made by G. Lunge and E. Schmid<sup>7</sup> regarding the action of nitric acid upon aluminum. They show that aluminum is readily attacked by nitric acid of 1.20 sp. gr. at ordinary temperatures, and that with nitric acid of sp. gr. 1.50 the action is comparatively feeble.

<sup>1</sup> The Properties of Aluminium, with Some Information Relating to the Metal. *Trans. Amer. Mining Engineers*, 18, 537.

<sup>2</sup> The Properties of Aluminium. *Electrical World*, 17, 390.

<sup>3</sup> Aluminium. *Nature*, 40, 185.

<sup>4</sup> Aluminium. *J. Frank. Inst.*, 126, 293.

<sup>5</sup> Action of Sulphuric and Nitric Acids upon Aluminium. *Chem. Ztg.*, Report., 15, 276; *Bull. Rouen*, 19, 232.

<sup>6</sup> Bull. U. S. Geological Survey, 1893; *This Journal*, 15, 221.

<sup>7</sup> *Ztschr. angew. Chem.*, 1892, 7.

The following table shows the results of the action of various strengths of nitric acid upon aluminum foil at ordinary temperature ( $20^{\circ}$  C.) ; duration of test being ten days.

| Specific gravity of nitric acid. | Experiment I.  |  | Experiment II.   |   | Average. | Average. |
|----------------------------------|--|--|--|---|----------|----------|
|                                  | Milligrams aluminum dissolved from 60 sq. centimeters. | Milligrams aluminum dissolved from 60 sq. centimeters. | Milligrams aluminum dissolved from 60 sq. centimeters. | Milligrams aluminum dissolved from 100 sq. centimeters. |          |          |
| 1.20                             | 615.0  | 617.7  | 616.4  | 1027.4  |          |          |
| 1.40                             | 242.7  | 236.9  | 239.8  | 399.7   |          |          |
| 1.50                             | 23.7   | 21.6   | 22.7   | 37.8  |          |          |

These experiments were conducted in the chemical laboratory of the Zurich "Polytechnicum."

The aluminum was in the form of sheet metal, cut into strips of eighty mm. long, twenty-seven mm. wide, and one mm. thick. Its composition was : Aluminum 99.2 per cent., iron 0.25 per cent., combined silicon 0.44 per cent., and crystallized silicon 0.11 per cent.

Messrs. Lunge and Schmid conclude as follows :

" Several experiments made by us convince us that the statements in the text-books, according to which aluminum is slightly or not at all attacked by  $HNO_3$ , are decidedly incorrect ; which fact brings to naught the hope entertained that this metal can be used in the manufacture of nitric acid."

In confirmation of these tests I made the following experiments, using aluminum (manufactured by the Pittsburg Reduction Co.) containing 99.6 per cent. of aluminum.

Coarse turnings were made of the metal, and six samples, each of one gram, were transferred to glass flasks and treated as follows :

#### EXPERIMENT I.

|                                       |                 |
|---------------------------------------|-----------------|
| Specific gravity of nitric acid ..... | 1.15            |
| Amount of acid taken .....            | 100 cc.         |
| Length of test .....                  | 7 days          |
| Temperature of acid .....             | $20^{\circ}$ C. |
| Per cent. of aluminum dissolved ..... | 94.2            |

I. Result = 94.2 per cent. aluminum dissolved.

#### EXPERIMENT II.

|                                       |                  |
|---------------------------------------|------------------|
| Specific gravity of nitric acid ..... | 1.15             |
| Amount of acid taken .....            | 100 cc.          |
| Length of test .....                  | 20 minutes       |
| Temperature of acid .....             | $100^{\circ}$ C. |
| Per cent. of aluminum dissolved ..... | 100              |

II. Result = 100 per cent. aluminum dissolved.

## EXPERIMENT III.

|                                      |         |
|--------------------------------------|---------|
| Specific gravity of nitric acid..... | 1.35    |
| Amount of acid taken.....            | 100 cc. |
| Length of test .....                 | 7 days  |
| Temperature of acid .....            | 20° C.  |
| Per cent. of aluminum dissolved..... | 89      |

III. Result = 89 per cent. aluminum dissolved.

## EXPERIMENT IV.

|                                      |            |
|--------------------------------------|------------|
| Specific gravity of nitric acid..... | 1.35       |
| Amount of acid taken.....            | 100 cc.    |
| Length of test .....                 | 30 minutes |
| Temperature of acid .....            | 100° C.    |
| Per cent. of aluminum dissolved..... | 100        |

IV. Result = 100 per cent. aluminum dissolved.

## EXPERIMENT V.

|                                      |         |
|--------------------------------------|---------|
| Specific gravity of nitric acid..... | 1.46    |
| Amount of acid taken.....            | 100 cc. |
| Length of test .....                 | 7 days  |
| Temperature of acid .....            | 20° C.  |
| Per cent. of aluminum dissolved..... | 100     |

V. Result = 12 per cent. aluminum dissolved.

## EXPERIMENT VI.

|                                       |         |
|---------------------------------------|---------|
| Specific gravity of nitric acid.....  | 1.46    |
| Amount of acid taken.....             | 200 cc. |
| Length of test .....                  | 2 hours |
| Temperature of acid .....             | 100° C. |
| Per cent. of aluminum dissolved ..... | 100     |

VI. Result = complete solution.

These results show that aluminum in the form of coarse turnings is readily acted upon by nitric acid, hot or cold, the solution of the metal being more rapid in nitric acid, of sp. gr. 1.15, than with the stronger acid of sp. gr. 1.45. In this connection, no doubt, the form in which the metal exists has a material influence upon the rapidity of solution in nitric acid.

If the metal be in thick plates the action of the nitric acid is very much retarded.

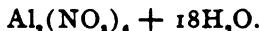
N. Menschutkin<sup>1</sup> considers that a layer of nitric oxide is formed, protecting the metal from further action of the acid.

To prove or disprove this statement, I selected a piece of aluminum (of the same composition as that with which the above experiments were made), one inch long, one inch wide,

<sup>1</sup> Analytical Chemistry, by N. Menschutkin, London, 1895, p. 65.

and one-half inch thick. This was placed in a large flask, 700 cc. of nitric acid, 1.35 sp. gr., added and kept at a temperature of 100° C., for five hours, when complete solution of the aluminum was effected. The result of these tests shows that while aluminum in thin foil, or coarse turnings, is easily dissolved in nitric acid, hot or cold, solution is materially retarded in hot nitric acid if the aluminum be present in thick plates, and that solution in cold nitric acid is practically *nil* under the same conditions.

The solution of aluminum nitrate which I obtained from experiment IV deposited crystals of aluminum nitrate in the form of colorless, truncated, rhombic, octahedral crystals, similar in composition to those described by Ordway,<sup>1</sup> of the composition



Ordway, however, obtained the aluminum nitrate by dissolving recently precipitated aluminum hydroxide in nitric acid and slowly concentrating, the crystals having the form of colorless rhombic prisms.

A. Ditte<sup>2</sup> describes a basic aluminum nitrate, obtained by the action of dilute nitric acid upon aluminum, of the composition  $\text{Al}_2(\text{NO}_3)_6 + 4\text{H}_2\text{O}$ . It exists as a white precipitate in the form of fine needles.<sup>3</sup>

I have failed to find in the bibliography of aluminum nitrate any reference to the formation of  $\text{Al}_2(\text{NO}_3)_6 + 18\text{H}_2\text{O}$  by the direct action of nitric acid upon aluminum, as obtained in experiment IV, above described.

DEPARTMENT OF ANALYTICAL CHEMISTRY,  
STEVENS INSTITUTE OF TECHNOLOGY.

<sup>1</sup> *Am. J. Sci.* (2), 9, 33.

<sup>2</sup> *Compt. rend.*, 110, 782.

<sup>3</sup> *Handbuch der anorganische Chemie*, Dammer, 3, 106.

## EARLY AMERICAN CHEMICAL SOCIETIES.<sup>1</sup>

BY H. CARRINGTON BOLTON.

Received July 19, 1897.

THREE chemical societies were organized in the United States before the close of the first quarter of this century; one as early as 1792, the second in 1811, and the third in 1821. These societies were short-lived, local in jurisdiction, and without much influence on the progress of the science, but it is interesting to note that professional, teaching, and amateur chemists in America formed associations for mutual improvement and for the advancement of their calling, long before their European brethren. The Chemical Society of London, the oldest in Europe, was founded in 1841, forty-nine years after the first American society; that of Paris dates back from 1858, and that of Germany from 1868. American chemists were not impelled to form independent societies owing to a lack of organizations for men of science, but they early felt the advantages of a specialized association. The society of 1792, and that of 1811, were both founded in a city honored by the presence of the venerable and dignified American Philosophical Society, established by Benjamin Franklin in 1743.

The existence of these societies has long been known, but only through casual references to them by writers on the beginnings of science in the United States; Prof. Benj. Silliman, in his essay on "American Contributions to Chemistry," read at the centennial celebration of the discovery of oxygen, held at Northumberland, in 1874, alludes to them incidentally, and Dr. Brown Goode, in his historical addresses to the Biological Society of Washington, barely mentions them.

The publications too, of the earlier societies, are very little known, being rarely found in the best libraries.

Under these circumstances it has seemed not altogether useless to summarize what information concerning these societies I have been able to gather, and to offer it as a contribution to the history of chemistry in the United States.

The three societies are :

I. The Chemical Society of Philadelphia, founded in 1792.

<sup>1</sup> Read before the Washington Chemical Society, April 8, 1897.

II. The Columbian Chemical Society of Philadelphia, founded in 1811.

III. The Delaware Chemical and Geological Society, founded in 1821.

I. THE CHEMICAL SOCIETY OF PHILADELPHIA.

The Chemical Society of Philadelphia was undoubtedly the earliest organized body of chemists in either hemisphere, having been "instituted" in 1792. The society does not seem to have published records of its meetings, nor of the papers presented thereat, and since at that early day the primitive local newspapers paid little attention to items of scientific interest, information concerning it is not readily obtained. I find, however, that it was flourishing in 1801-2, when it had the following officers :

*President*—Dr. James Woodhouse.

*Vice-presidents*—Felix Pascalis and John Redman.

*Librarian*—William S. Jacobs.

*Curators*—William Brown and John S. Dorsey.

*Treasurer*—John Y. Bryant.

*Secretary*—Thomas Brown.

The society held stated meetings each week.

The President of the society, Dr. James Woodhouse (1770-1809), was at the time professor of chemistry in the medical department of the University of Pennsylvania, of which he was a graduate.

This chair had been held by Dr. James Hutchinson, and on his death, in 1793, Dr. Joseph Priestley, who arrived from England a few months later, was invited to succeed him, but he declined, preferring the quiet life of Northumberland, and Dr. Woodhouse was chosen instead. Dr. Woodhouse contributed several medical papers to the New York Medical Repository, and to Coxe's Medical Museum; he also edited Chaptal's Elements of Chemistry (fourth edition, 1807, 2 vols.), and Parkinson's Chemical Pocket-Book (1802). He is said to have been the first to prove by comparative experiments the superiority of anthracite coal from Pennsylvania over bituminous coal from Virginia for intensity and regularity of heating power. (Silliman.)

The first vice-president, Felix Pascalis Ouvrière (1750-1840), had an interesting career. He was born in France, where he received his medical education; he emigrated to Santo Domingo, and while practising medicine there acquired an extensive knowledge of botany and other branches of natural history. In 1793 a revolt among the negroes compelled Pascalis to flee and he took refuge in the United States, first at Philadelphia, and later at New York, where he resided more than thirty years. He was the founder of the Linnæan Society of New York, and the author of several medical papers and reports.

The second vice-president, Dr. John Redman, (1722-1808), was a native of Philadelphia, and educated in European medical schools and hospitals. In 1786 he was made president of the Philadelphia College of Physicians. He was regarded as one of the foremost practitioners of medicine of Philadelphia, but his methods now appear super-heroic.

Dr. John Syng Dorsey (1783-1818), one of the curators, was professor of surgery and afterwards of *materia medica* in the University of Pennsylvania. He had a high reputation as a surgeon, but his qualifications for membership in a chemical society seem to have been based chiefly on the fact that in his youth he had attended the chemical lectures of Sir Humphry Davy (1803).

I have not found the roll of members of this early society, but it appears that Priestley, Hare, and Seybert were active in it. The ambition of the members is shown by the circumstance that in 1802 there was a standing committee prepared to "annualize every mineral production" brought before them and to give "an accurate account of each specimen free of expense."

The meeting held October 24, 1801, was made memorable by the appointment of a committee for the "discovery of means by which a greater concentration of heat might be obtained for chemical purposes." On this committee was placed among others Robert Hare, then only twenty years of age; but so soon as December 10th of the same year, he reported to the society, on behalf of the committee, his invention of the "hydrostatic" (oxy-hydrogen) blowpipe. I need not here eulogize this important and useful invention, which yielded such a fruitful harvest of discoveries. This alone justified the existence of the

first of chemical societies. In the following year the society caused Dr. Hare's account of this blowpipe to be printed in a pamphlet of thirty-four pages, 12mo., with one plate. This now rare booklet bears the title : "Memoir on the Supply and Application of the Blowpipe, containing an account of a new method of supplying the blowpipe either with common air or oxygen gas; and also of the effects of the intense heat produced by the combustion of the hydrogen and oxygen gases. Illustrated by engravings. Published by order of the Chemical Society of Philadelphia, to whom it was presented by Robert Hare, jun., Corresponding Member of the Society. Philadelphia. Printed for the Chemical Society by H. Maxwell, Columbia House, 1802."

Robert Hare's subsequent career as professor of chemistry in the medical school of the University of Pennsylvania from 1818 to 1847, is well known and accessible to all inquirers.

How much longer this association of chemists continued to meet, I have not ascertained. But the work of this society was evidently remembered by those who, ten years later, founded a new one, inasmuch as they designated it by the prefix "Columbian" to avoid confusion.

## II. THE COLUMBIAN CHEMICAL SOCIETY OF PHILADELPHIA.

The Columbian Chemical Society was founded in the month of August, 1811, by "a number of persons desirous of cultivating chemical science and promoting the state of philosophical inquiry." The names of the gentlemen who attended this meeting are not certainly known, but it may be presumed that they included most of those who were then elected to office; these were as follows :

*Patron*—Hon. Thomas Jefferson, Esq.,

*President*—Prof. James Cutbush,

*Vice-presidents*—George F. Lehman and Franklin Bache,

*Secretary*—John C. Heberton,

*Treasurer*—James J. Hamm,

*Orator*—John R. Barnhill,

and a "Corresponding Committee" of three: John Barnes, M.D., John Lynn, M.D., and Charles Edwards.

Thomas Jefferson's commanding position in the world of

<sup>1</sup> A copy of this is found in the Army Medical Library, Washington, D. C.

science and arts, as well as his literary attainments, well qualified him for the dignified office of patron. He had held the office of president of the most prominent scientific body in the United States (American Philosophical Society) for many years, and only relinquished it to accept the higher one of Chief Magistrate of the Nation. Seventeen months before the founding of the Chemical Society, Jefferson had retired from the presidency, after serving his country eight years, and was living at his country seat, Monticello.

James Cutbush, president of the Columbian Society, was at that time professor of natural philosophy, chemistry, and mineralogy at St. John's College. Little is known of his early history; in 1814 he was appointed to the army with rank of Assistant Apothecary General, and he held the position of chief medical officer of the United States Military Academy at West Point, from June, 1820, to November, 1821; the army being reorganized, he became assistant surgeon and acting professor of chemistry and mineralogy at the same institution, positions which he held until his death, December 15, 1823.

Dr. Cutbush's papers, presented to the Columbian Society, will be considered below; he published also the following: "On the Formation of Cyanogen in Some Chemical Processes Not Before Noted,"<sup>1</sup> "On the Composition and Properties of the Chinese Fire,"<sup>2</sup> "On the Composition and Properties of Greek Fire."<sup>3</sup> He was also the author of several books: "Useful Cabinet," (1808); "Philosophy of Experimental Chemistry," (Philadelphia, 1813), and "A System of Pyrotechny," (Philadelphia, 1825). The last named is an elaborate work of more than 600 pages, octavo.

George F. Lehman, the first vice-president, published articles in Mitchill's Medical Repository, chiefly on medical subjects.

Franklin Bache, the second vice-president, was at that date a youth of only twenty years, who had graduated at the University of Pennsylvania the year before the founding of the society. He was a grandson of Benjamin Franklin and a member of the distinguished Bache family, which numbered so many eminent

<sup>1</sup> *A.M. J. Sci.*, 6, 1822.

<sup>2</sup> *Ibid.* 7, 1823.

<sup>3</sup> *Ibid.* 6, 1822.

men of science. He afterwards became professor of chemistry at the Franklin Institute, and in 1841 at the Jefferson Medical College, which chair he held until his death in 1864. He is remembered also as the author of "A System of Chemistry for the Use of Students of Medicine," (Philadelphia, 1819), and of other chemical treatises.

The constitution adopted by the founders of the society, besides the usual provisions for regulating business, contained some unusual features; the officers included an orator, and Article VII prescribed: "An oration on some chemical subject within two months after the commencement of the medical lectures in the University of Pennsylvania, in each year." Since the "Memoirs" published by the society contain no "oration," it is to be feared that the incumbent's efforts were not satisfactory.

Two articles in the constitution deal with fines; "Every member shall be fined  $12\frac{1}{2}$  cents for absence each roll, unless satisfactory reasons be offered;" and again: "Any member being elected to office and refusing to serve, shall be fined one dollar."

Another notable provision is as follows: "The society shall appoint, once in each month, some member to read an original chemical essay, for neglect of which, the member so appointed shall be fined one dollar." These fines, with the annual fee of two dollars, were evidently expected to maintain a full treasury.

To become a member of the society, special qualifications were prescribed; after being proposed and seconded, the candidate "shall read an original essay on some chemical subject, on which any member may speak not more than ten minutes." After this trial of his ability, a two-thirds vote of the members present at a subsequent meeting were required to secure election.

It seems to have been easier to be put out of the society than it was to get in, for "any member behaving in a disorderly manner, shall be expelled by consent of two-thirds of the members present."

This mandatory "shall" is used throughout the regulations; the president "shall preserve order," the secretary "shall keep fair minutes," the constitution "shall be revised annually," and so on. To insure against members withdrawing early from

a dull meeting, the "Secretary shall call the roll at the opening and close of each meeting and mark down absentees," each of whom is then fined  $12\frac{1}{2}$  cents as stated. Never did a society undertake to control its members with more stringent rules!

The members who subscribed to these regulations were divided into two classes, "Junior" and "Honorary" members, the former corresponding to a class which would now be styled "Associates," and the latter including both American and foreign chemists of distinction. The junior members numbered thirteen, the honorary members numbered sixty-nine, thirty-one of whom were Europeans. The home list included most of those chemists then living in America, whose labors contributed largely to the foundations of the science in the New World. Brief notices of some of the members will serve to summarize the status of chemistry in the United States for the years 1811-1813.

Dr. Benjamin Smith Barton (1766-1815), held the chair of medicine, natural history, and botany in the University of Pennsylvania. Dr. Barton has been called by his admirers, "the father of American natural history," though there are other claimants for this honorable designation, Mitchill, of New York, and Thomas Jefferson. Dr. Brown Goode, writing of Barton, says he, of all the early Philadelphia naturalists, "had the most salutary influence on the progress of science." He was a leader in the American Philosophical Society, and an agreeable writer on natural history topics, and though he made no contributions to chemistry, was a worthy member of the society.

Dr. Archibald Bruce (1777-1818), one of the pioneers of mineralogical science in America; he had established the American Mineralogical Journal, one year before the date of which I write. His analyses of minerals mark him as a skilful chemist. He held the chair of mineralogy in Columbia College, New York.

Joseph Cloud (1770-1845) was assay master of the United States Mint in Philadelphia, and already distinguished by his researches on palladium (1807).

Thomas Cooper (1759-1840), born in London, had come to America in 1792, with his friend Priestley, whose radical views in politics and religion he shared. Dr. Cooper wrote much on political, ethical, and philosophical subjects, and published some

essays on chemistry. In 1811-14, the period of the Columbian Chemical Society, he held the chair of chemistry at Dickinson College, Carlisle, Pa., and in 1819-34 he held the same position at the College in Columbia; S. C., of which he afterwards became president.

Dr. John Redman Coxe was professor in the medical department of the University of Pennsylvania, having succeeded Dr. Woodhouse. He made several original observations in chemistry published in current periodicals.

Dr. Edward Cutbush (1772-1843) was surgeon of the United States Navy and professor of chemistry in the medical school of the Columbian University, Washington (1825-27). He has another honorable claim to distinction, having been the founder in 1819 of the Columbian Institute for the Promotion of Arts and Sciences in Washington, a sort of precursor of the Smithsonian Institution.

Passing with brief mention Dr. Elisha de Butts, professor of chemistry in the College of Maryland, Prof. Benjamin de Witt, of New York, and Dr. John Syng Dorsey, already mentioned as a member of the society founded in 1792, we reach the more familiar name of Dr. John Griscom, "the acknowledged head of all teachers of chemistry in New York City," for more than thirty years.

The next name in the alphabetical list of members is that of Robert Hare, professor of natural philosophy in the University of Pennsylvania, whose career we have already noticed.

Dr. David Hosack (1769-1835), professor of botany and *materia medica* in Columbia College, New York, is best known as the founder of the first public botanic garden in the United States, in 1801. His contributions to science were chiefly in medicine. The tragic circumstances of his death have been nearly forgotten ; he died of shock at the disastrous conflagration in New York City in 1835, which swept away his property to the value of \$300,000.

Dr. Henry Jackson, professor of chemistry at Athens College, Georgia, is followed by His Excellency, James Madison, LL.D., President of the United States of America, whose name added luster to the rolls of the society, but whose claim to the membership can only be based on extensive general information.

Dr. John Manners, of Philadelphia, affixes to his name the initials F.A.N.S., the Academy of Natural Sciences, having been founded one year before the printing of the list of members. His contributions to the Chemical Society will be noted below.

Dr. John Maclean, (1771-1840), was the first professor of chemistry in the College of New Jersey, now Princeton University, to which chair he was elected in 1797. In accordance with the prevailing custom, he also gave the instruction in astronomy, mathematics, natural philosophy, and natural history; this fact is ample apology for his not appearing in the ranks of original investigators. Prof. Maclean published in 1797, "Two Lectures on Combustion," in which he upheld the views of Lavoisier, as opposed to the phlogistic theory maintained by Dr. Priestley.

The Hon. Samuel L. Mitchill, M.D., F.R.S.E. (1764-1831), professor of chemistry and natural history in Columbia College from 1792, was active in many branches of scientific research. In 1798 he established the New York Medical Repository, which for sixteen years was an influential organ in recording and diffusing progress in general science, as well as in medicine. His zeal for science did not prevent his taking part in national affairs, for he occupied a seat in the senate of the United States from 1804.

Dr. Thomas D. Mitchell, F.A.N.S., was one of the most active members of the society, frequently contributing to its memoirs.

Passing by Dr. John C. Osborne, professor of the institutes and practice of medicine in Columbia College, New York; Dr. Joseph Parish, of Philadelphia; Mr. Robert Patterson (1743-1824), professor of mathematics and lecturer on natural philosophy in the University of Pennsylvania, director of the United States Mint, and afterwards (1819) president of the American Philosophical Society; Dr. Nathaniel Potter, professor of the theory and practice of medicine, University of Maryland, we reach the eminent Dr. Benjamin Rush, professor of the institutes and practice of medicine in the University of Pennsylvania. Dr. Rush (1745-1813) has been characterized by Benjamin Silliman as "undoubtedly the first Professor of Chemistry in America," his appointment dating August 1, 1769. In his

busy life, besides his professorial chair, he filled the positions of surgeon-general of the United States Army (1777), treasurer of the Mint, president of the Society for the Abolition of Slavery, vice-president of the Bible Society of Philadelphia, and conducted a large medical practice in the same city.

Dr. Adam Seybert (d. 1825), was one of the earliest American chemists to make a series of analyses of the air by eudiometric methods. Having made twenty-seven air analyses during a voyage across the Atlantic, he compared the results with others made on land and drew the conclusion that the sea exerted purifying power over the air; his paper before the American Philosophical Society bore the date 1797.

Benjamin Silliman is a name so familiar to American chemists as to require no eulogium in this place. At the founding of the chemical society he was forty years of age and had held the chair of chemistry in Yale College for ten years. It should be remembered that he did not begin publishing the American Journal of Science until 1818.

Dr. John S. Stringham, professor of chemistry in New York, (institution not specified); Dr. Jared Trout, (whose name should be written Gerard Troost), lecturer on mineralogy in the Academy of Natural Sciences, Philadelphia, and afterwards professor of chemistry, mineralogy, and geology in Nashville University (1828-50); Lawrence Washington, Esq., of Virginia, and Dr. Caspar Wistar, professor of anatomy in the University of Pennsylvania, with his relative Charles Wistar, complete the roll of home members.

The prominence of medical men on this list is evident, and is easily explained. Before the days of schools of science, and before colleges devoted a portion of their curricula to scientific studies, almost the only training in science received by American youth was in the medical schools. The chairs of natural history and of the physical sciences were almost exclusively held by physicians whose education more nearly qualified them for teaching these branches of knowledge than the graduates of the classical courses customary in all colleges.

To elevate the standard of membership in the Columbian Chemical Society, a number of distinguished foreigners were enrolled. France contributed Adet, Berthollet, Chaptal, Dey-

eux, Abbé Hauy, Bouillon-Lagrange, Gay-Lussac, Monge, Guyton de Morveau, Parmentier, Pelletier, Sequin, Thénard and Vauquelin. Great Britain was represented by Sir Joseph Banks, John Dalton, Sir Humphry Davy, John Davy, J. A. de Luc, Hatchett, Dr. William Henry, Sir William Herschel, Dr. John Hope, John Murray, William Nicholson, Dr. G. Pearson, Mr. W. H. Pepys, Dr. Thomas Thomson, Alexander Til-loch and Dr. William Hyde Wollaston. Spain was represented by Professor Proust of Madrid, and the other countries of Europe had not a single representative. The absence of such eminent names as Richter, Klaproth, Stromeyer, Trommsdorff and Gehlen, of Germany, as well as of Berzelius, the Swede, presumably indicates that at this early date, communication and exchange of courtesies with Germany and Northern Europe was less common than with England and France.

The Columbian Chemical Society of Philadelphia published in 1813 one volume of Memoirs;<sup>1</sup> this forms a book of 221 pages, octavo, and bears the imprint of Isaac Peirce, No. 3 South Fourth Street, Philadelphia. It contains twenty-six essays, by ten writers, on a great variety of topics, original, speculative and practical.

No less than eight of the papers are from the pen of Dr. Thomas D. Mitchell, and these I proceed to review. Dr. Mitchell's "Remarks on the Phlogistic and Antiphlogistic Systems of Chemistry" opens the volume; in this essay he supports the Lavoisierian theory of combustion, stating that there is "no necessity for the principle of inflammability;" he cites the experiment of Woodhouse, who obtained an inflammable air by heating charcoal with scales of iron, both being free from water, and points out that Cruikshank, of Woolwich, demonstrated that the inflammable gas thus obtained is gaseous oxide of carbon (carbon monoxide), discovered by Priestley in 1799, and combustible, although containing no hydrogen. He compares combustion with neutralization of an acid and base, saying: "Inflammation and acidity are effects resulting from the action of relative causes, and not attributable to a single agent or principle."

Dr. Mitchell's second paper, "Remarks on Heat," deals with

<sup>1</sup>Copies of the Memoirs are found in Philadelphia libraries, and in the private library of the writer.

speculations on latent heat, objecting to this term and to Dr. Black's theories.

In a paper entitled "On Muriatic and Oxy-Muriatic Acids," Dr. Mitchell vehemently attacks the views of Sir Humphry Davy as to the non-existence of oxygen in muriatic acid, clinging to the statement of Lavoisier, that all acids contain oxygen. In a section on combustion, he remarks, "we have incontestible proof that oxygen gas contains light," and he regards combustion as accompanied by the decomposition of oxygen gas.

Dr. Mitchell's fourth paper is of a more practical character, being the "Analysis of Malachite" from Perkioming, Pennsylvania. The result is given as follows: "120 grains of the green carbonate contained carbonic acid, 30 grains; quartz and silicious earth, 68 grains; brown oxide of copper, 15 grains; loss in the process, 7 grains."

The specimen was evidently a poor one; no account was taken of the water, and reporting results in percentages was not in vogue.

In some "Remarks on Putrefaction," the same writer discusses the action of antiseptics, and attributes the virtue of nitrate of potash to the increase of cold produced by the muriate of soda.

Dr. Mitchell's "Chemical View of Secretion," and his "Analysis of Professor Coxe's Essay on Combustion and Acidification," are polemical and speculative; in his "Remarks on the Atmosphere" he argues to prove the atmosphere a chemical union of oxygen and nitrogen.

Franklin Bache contributes three essays to the volume. "An Inquiry into What Circumstances Will Warrant us Justly to Reckon any Substance a Principle of a Common Property of Any Set of Bodies," discusses the much disputed question of that day, whether hydrogen as well as oxygen can be an acid-forming principle. His conclusion being, "it may." Bache's second paper is entitled, "An Inquiry Whether Mr. Berthollet was Warranted from Certain Experiments in Framing the Law of Chemical Affinity, that it is Directly Proportional to the Quantity of Matter." In this essay the author points out "the probable way in which this great philosopher fell into this great error." In a third paper styled "Thoughts on the Expediency of

Changing Parts of the Chemical Nomenclature," Mr. Bache proposes the following names: Nitral acid forming nitrotes, nitril acid forming nitrutes, nitrous forming nitrites, and nitric acid forming nitrates, for the several acid-forming oxides of nitrogen. Fortunately his influence was insufficient to inflict these names on chemical language.

Dr. John Manners contributed four papers to the Memoirs. (1) "Experiments and Observations on the Effect of Light on Vegetables and upon the Physiology of Leaves," which abounds in quotations from Darwin's "Botanic Garden." (2) "Analysis of a Mineral Spring at the Willow Grove," (fourteen miles from Philadelphia). In this the author was assisted by Dr. Mitchell. They report the action of each testing solution on the water, and conclude that the water contains iron and sulphuretted hydrogen, and show the absence of lime, copper and carbonic acid." (3) "On the Production of Sulphuretted Hydrogen by the Action of Black Sulphuric Acid, Diluted with Water on Iron Nails." The acid had been blackened by a piece of cork which had fallen in. (4) "Experiments and Observations on Putrefaction." In this paper Dr. Manners tested the influence of carbonic acid, hydrogen and other gases on putrefying flesh, and also attempted to collect and analyze the gases generated by the same. He concludes that "putrefaction depends on a destruction of the equilibrium of attractions which exists in the elementary principles of which the animal substance is composed in a healthy state, occasioned by the loss of vitality in consequence of which new compositions and decompositions ensue."

Professor Cutbush, President of the Society, wrote "On the Prognostic Signs of the Weather," and "On the Oxyacetite of Iron as a Test for the Discovery of Arsenic;" the latter being a good presentation of his discovery, subsequently used as a quantitative method by Kotschoubcy.

Mr. Samuel F. Carl, one of the junior members, has two papers containing analyses, the first of the mineral spring at Bordentown, New Jersey, which proved to be a "carbonated chalybeate water," and the second of two specimens referred to him by the society; these proved to be respectively an iron ore

and a ferruginous copper ore. The method of reporting results seems very crude to a modern analytical chemist.

Dr. Joel B. Sutherland contributes "Speculations on Lime," in which he claims that if mortar be made with sand containing common salt, the resultant compound gives so much coldness to the mass that during the whole summer vapor is almost incessantly precipitated on the wall with which it is plastered. He also wrote "A Few Remarks on the Nature of the Nervous Influence." Akin to the latter are the "Thoughts on the Principle of Excitability," by George Ferdinand Lehman, who also wrote "On the Emission of Oxygen by Plants."

Mr. William Hembel, Jr., has two papers, one entitled "Observations on the Formation of Muriate of Potash in the Process of Preparing the Hyperoxymuriate of Potash," which is complicated by the belief that hydrochloric acid is an oxygen compound; and another entitled "A New Method of Mounting Woulfe's Apparatus," which is unintelligible owing to the omission of a woodcut to which the text refers.

Mr. Edward Brux, of France, one of the junior members, writes "Upon the Effects of Various Gases upon the Living Animal Body," which consists largely of speculations: notwithstanding which he cites an admirable passage from Dr. Bostock; "Physiologists have, in general, been more inclined to form hypotheses than to execute experiments, and it has necessarily ensued from this unfortunate propensity that their science has advanced more slowly than perhaps any other department of natural philosophy." Unfortunately this truth was not fully recognized by the members of the Columbian Chemical Society.

A contemporary journal (N. Y. Medical Repository), in reviewing the "Memoirs," uses the following quaint language: "It is highly gratifying to behold a band of worthies like those before us, laboring to analyze the compounds which they find ready made, to form by synthesis new combinations in the laboratory, and thereby to deduce correct doctrines from the facts which are disclosed. We cordially congratulate them on their noble occupation and on the progress they have made. We hope they will be persevering and undaunted. And if from this beginning there shall arise great improvements in theoretical disquisition, as well as in economical exercise, we shall rejoice

with a mingled glow of amicable and patriotic sentiment."

### III. THE DELAWARE CHEMICAL AND GEOLOGICAL SOCIETY.

The Delaware Chemical and Geological Society was organized at Delhi, Delaware County, New York, September 6, 1821; the first meeting was held at the hotel of G. H. Edgerton in the village, and the following officers were chosen:

*President*—Charles A. Foote.

*Vice-President*—Rev. James P. F. Clark.

*Recording Secretary*—Charles Hathaway.

*Corresponding Secretary*—Dr. Calvin Howard.

*Treasurer*—Selah R. Hobbie.

*Directors*—Cornelius R. Fitch, R. W. Stockton, Ebenezer Steele.

The society was composed of "between forty and fifty well-informed and respectable inhabitants" of the County of Delaware. The following gentlemen were elected corresponding members: Colonel Henry Leavenworth, U. S. A.; Edwin Crosswell, of Catskill, and O. Rice, of Troy.

The society had for its object the improvement of the members in literature and science, especially in chemistry and mineralogy. The members planned to form a library and to secure a chemical laboratory; they made a collection of the minerals and rocks of the region, which was still preserved in the Delaware Academy in 1856. The meetings of the society were held quarterly, and at each an essay or an "original scientific discourse" was presented; it was, however, not long sustained.

In reviewing the condition of chemical science in the United States, as indicated by the membership and achievements of these early societies, we note that those who held the most prominent places were handicapped by the necessity of devoting a large part of their intellectual energy to topics quite outside of the domain of chemistry itself. The active members were either busy with the art of healing, or with teaching several branches of the physical and natural sciences, and too often chemistry was regarded in the colleges as a kind of side issue, or appendix to the more important subjects of instruction. This was caused

by the necessity of earning a competence at a time when there was no opportunity of reaping pecuniary rewards by skill as an analyst, or by the application of science to the manufacture of products involving chemical knowledge. Indeed, in default of this stimulus to laboratory work, it is not surprising that the papers read to the societies were largely either reviews of the grand discoveries made by Europeans, or essays in which the imaginative faculty was given free play, it being far easier to indulge in speculation than to discover new facts.

In the early struggles of a country to secure a place among nations, few men of ability can devote their energies to the pursuit of science for science's sake ; the environment is more favorable to development of the inventive faculty than of the peculiar talent for conducting abstruse researches in an exact science. Add to this the limited facilities for acquiring chemical knowledge in the New World, and the distance of amateurs from the European head-centers of learning, and it is certainly noteworthy that American chemists combined to form associations for mutual improvement and the advancement of their calling at so early a period.

A fourth attempt to establish a chemical society was made at New York City in 1876 ; the organization was at first somewhat restricted in its plan, but in 1892 a change in its constitution was effected, which broadened its scope, and it now forms a strong, influential and truly national society. Its 1196 members, working in nine chartered sections, represent forty-seven states and territories, besides several countries of Europe, South America, and distant Australia. Its Journal, comprising 1150 pages annually, is an authoritative medium for the preservation and diffusion of the researches made in the United States, and its annual meetings, held in diverse localities, strengthen the bonds which unite its members in good fellowship, and in the pursuit of their common profession. *Long may the American Chemical Society continue in its prosperous career!*

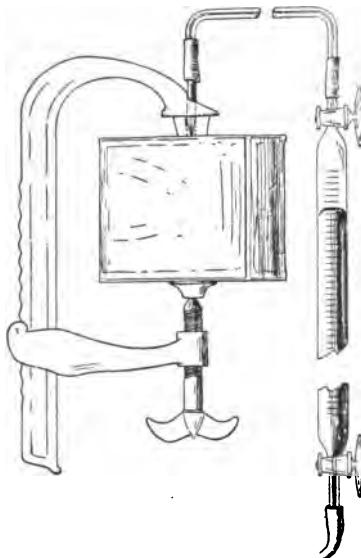
## METHOD OF COLLECTING AND ANALYZING THE GASES IN CANNED GOODS.<sup>1</sup>

BY CHARLES A. DOREMUS.

(Second paper.)

Received July 12, 1897.

THE first paper on this subject was read at the Second International Congress of Applied Chemistry, held last summer in Paris. As the publication of the proceedings has been delayed and would not reach some to whom this topic may be of interest, additional tests and analyses have been made and the accompanying illustration will possibly induce others to experiment further.



The first analyses of the gases in canned goods were effected in a Wilkinson gas analysis audiometer. This instrument is similar in form to a Lunge's nitrometer. The graduated tube has a glass stop-cock at its upper extremity, above which is a detachable funnel. A large inverted funnel was joined to the lower end of this instrument, and the whole filled with water in a pneumatic trough. The can was punctured beneath the funnel.

<sup>1</sup> Read before the New York Section, June 11, 1897.

The bubbles of gas rose through the water and were measured and analyzed.

This operation was inconvenient. It permitted the gases to come into contact with much water in which some portion of gas might readily dissolve.

These inconveniences are overcome by the aid of the following device. A beveled, hollow, steel needle is attached to the upper arm of an adjustable clamp. The point and lower part of the shaft are covered by a rubber stopper, which serves as a soft pad; the lower arm is moved along the body of the clamp until the can to be pierced is held between the rubber stopper and the head of the screw. The upper part of the needle is connected by means of a capillary tube filled either with water or mercury, with a receiver also filled with either of these liquids. The receiver may be either a stop-cock eudiometer as just described, or a eudiometer with leveling tube attached.

The apparatus adjusted, a turn or two of the screw clamps the can tightly between the rubber pad at the top and the screw head below. The rubber yields to the pressure, making a tight joint around the needle. When the latter pierces the tin the contained gases of the can escape gently into the eudiometer.

Cans containing sound goods present a collapsed condition, owing to the condensation of the steam after processing. "Rattlers" are cans which yield to pressure. "Swells" are cans which seem ready to burst. Enough gas can generally be obtained from either of the above for systematic analysis. Sixty to eighty cc. of gas can often be collected. The internal pressure is sometimes sufficient to split a seam and allow some of the contents to escape, or to burst a can with violence.

After collecting the gases the can should be opened and its contents carefully examined. A putrid odor indicates, of course, decomposition. Where this is absent and the food appears perfectly sound and undecomposed the distention may be due to different causes.

A bacteriological examination is advisable.<sup>1</sup> Through the kindness of Dr. Lederle, of the Board of Health, samples of various canned goods have been sent me and submitted to analysis.

<sup>1</sup> Putrefaction of Albumins, O. Emmerling: *Ber. d. chem. Ges.*, 29, 2721-2726.

Carbon dioxide forms the chief constituent of the gaseous mixture where putrid odor abounds. In other cases hydrogen predominates. The contents of the cans show little change. There is no offensive odor. There is absence of bacteria. There are positive indications of the corrosion of the inner metallic surfaces. Sometimes there is a discoloration of the can as if a slight amount of hydrogen sulphide had been formed. The contents of such cans also yield the reactions of the metals. Hydrogen has also been found where the evidences of corrosion were not marked. With the above clues afforded by the inspection of the contents of the can, the gases in the eudiometer may be subjected to the action of proper reagents in such order as to determine at least the main constituents. The reagents may be allowed to enter the stop-cock eudiometer, or the gases be transferred to pipettes as is customary in gas analysis. The recognition of traces of substances whose odor is very marked is difficult; for some we have no adequate tests.

COLLEGE OF THE CITY OF NEW YORK.

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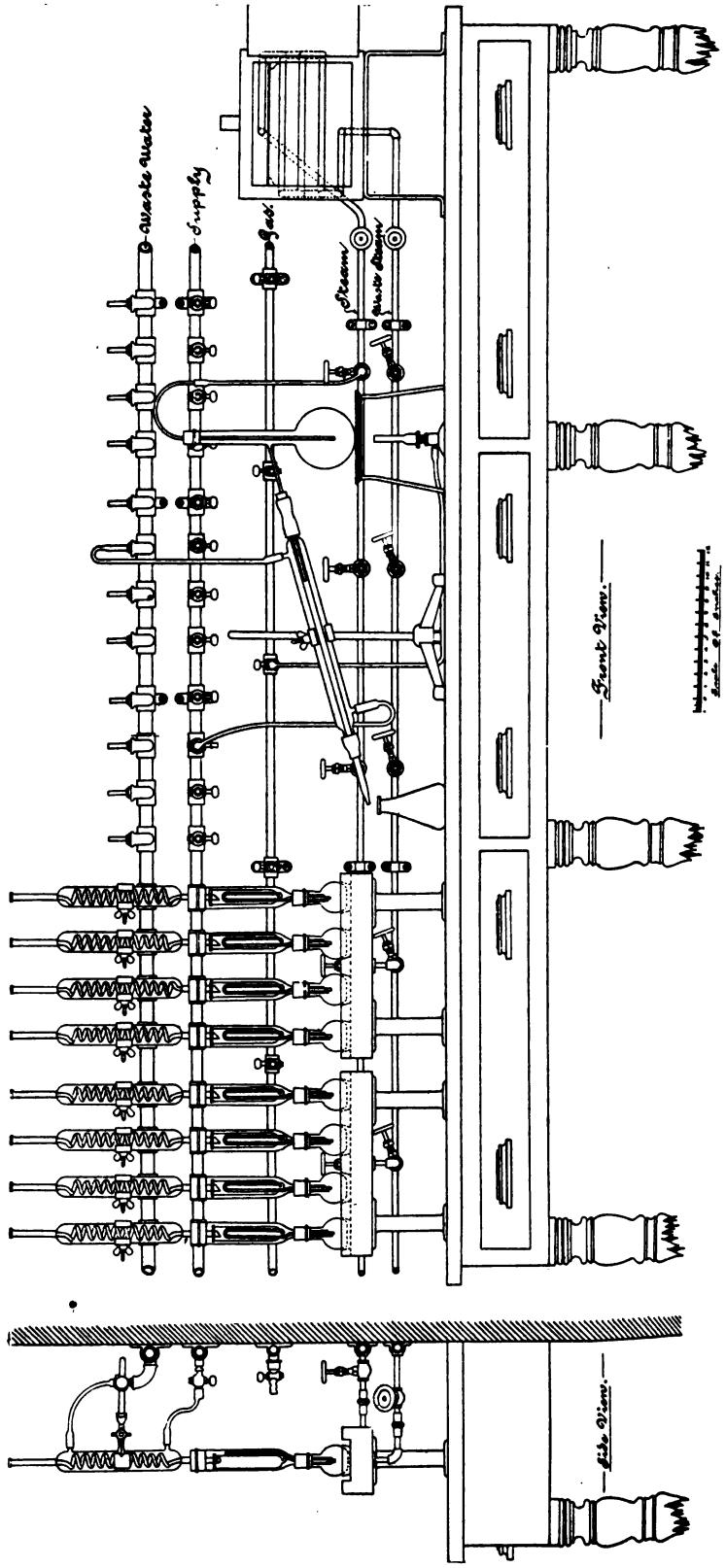
### MECHANICAL ARRANGEMENT OF FAT EXTRACTION APPARATUS.

BY G. J. VOLCKENING.

Received July 17, 1897.

THE apparatus shown in the accompanying drawing has been in use in the Chemical Laboratory of the Brooklyn Health Department for the past eighteen months. It was designed to meet the demand often experienced in food laboratories where large numbers of samples of milk are submitted for analysis. Too often is the chemist given an unoccupied room of no apparent use for other purposes and is told to build a laboratory. The disadvantage of a small laboratory was experienced. A separate room could not be given up for fat extraction; consequently this work had to be performed in the general and only room in the presence of naked flames. It was, therefore, necessary to produce a piece of apparatus that was compact, free from any chance of explosion, of a capacity sufficient to meet all demands and simple enough to be operated by the laboratory boy. About two feet above the table, on the wall, is

## Mechanical Arrangement Of Fat Extraction Apparatus.



fastened the waste pipe, which receives the water after it has passed through the condensers. In order to obviate any back pressure the pipe is made larger and carried direct to the sewer, without receiving the discharge from any other fixture. The inlet tubes are built up by using a T, an elbow, reducer, and short brass pipe about three inches long. The condensers are supported by clamps to these inlet tubes. The overflows from the condensers are connected by means of rubber tubing to the inlet tubes, which serve a double purpose; that of posts supporting the apparatus, and at the same time acting as outlets for the waste water.

The cold water supply pipe is securely fastened to the wall about six inches below and parallel to the line of waste. As the building was not supplied with a tank, the pressure in the general house supply often dropped below ten pounds. It was found necessary, in order to maintain a constant supply of water at all times, to run a separate line of pipe from the street direct to this table without being connected to any other fixture. There are twenty outlets on the table, each being provided with a separate stop-cock directly under the inlet tube of the waste; consequently each condenser can be operated independently of the others. Thus the number used at any time will depend upon the amount of work on hand.

The ether is heated on gun-metal steam tables, which have been tested up to a pressure of fifty pounds per square inch. In order to give closer contact and thus reduce the time of the operation, small capsules are placed on the table and partly filled with water. The bottoms of the flasks coming in contact with the hot water shortens the time of vaporizing the ether. As a substitute for the capsules a piece of thin felt moistened with water will answer the same purpose. Each steam table will support four sets of extractors. It will be seen by referring to the drawing that each table can be operated independently by means of the separate stop-cocks, and further, if only one table is required the others can be removed with their accompanying apparatus, thus allowing the space to be occupied for other purposes. The steam is generated by an upright tubular boiler heated by gas.

The whole or part of the laboratory table can be used for

other operations by disconnecting the apparatus. The drawing shows the table as it is used during the winter months, three steam tables being removed and in their place apparatus set up for steam distillation.

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### THE COMPOSITION OF HUMUS.

BY HARRY SNYDER.

Received July 6, 1897.

THE organic compounds of the soil to which the term humus is collectively applied, are a group about which but little is actually known. The humus compounds have not been extensively studied because of the difficulty of separating and obtaining them in a pure state. They do not form well-defined crystalline compounds, and they are all about equally soluble in various reagents. In fact, the analyst, when working with the humus compounds, is never sure whether he is working with a single compound or a mixture of several compounds.

The usual method employed in soil analysis for the determination of the humus compounds is the Grandjeau or some modification of that method, which consists of first treating the soil with cold dilute hydrochloric acid to remove the lime, and then, after washing with distilled water, extracting the humus materials with a dilute ammonia solution. The humus extract is evaporated to dryness, dried, weighed, ignited, weighed again, and the loss of weight calculated as humus.

Inasmuch as the organic compounds of the soil may be derived from so many different sources, as any form of decayed animal or vegetable matter, it must necessarily follow that humus is very complex in composition. It seemed best, in this study of the composition of humus, to produce the humus from known materials, rather than to start with humus from unknown sources. Humus was prepared in the following way: A soil containing only a small known amount of organic material was used. About 200 grams of sugar were mixed with 3,000 grams of soil, placed in a tight box, and allowed to undergo humus formation, out of doors, for one year. Humus was produced in this way from a variety of materials, as cow manure, green clover, meat scraps, wheat flour, saw dust, oat straw, and sugar.

The humus materials produced from these various substances were obtained by extracting the soil, after treatment with dilute hydrochloric acid and distilled water, with a three per cent. potassium hydroxide solution. The alkaline humus extracts were neutralized with hydrochloric acid, which gave black and brown precipitates of humus materials, which were washed, dried, and prepared for analysis. The precipitated humus materials contained from five to twelve per cent. of ash, and had the following ultimate compositions, on an ash-free basis:

## HUMUS PRODUCED BY

|              | Cow manure.<br>Per cent. | Green clover.<br>Per cent. | Meat scraps.<br>Per cent. | Wheat flour.<br>Per cent. | Oat straw.<br>Per cent.  | Saw-dust.<br>Per cent. | Sugar.<br>Per cent. |
|--------------|--------------------------|----------------------------|---------------------------|---------------------------|--------------------------|------------------------|---------------------|
| Carbon.....  | 41.95                    | 54.22                      | 48.77                     | 51.02                     | 54.30                    | 49.28                  | 57.84               |
| Hydrogen.... | 6.26                     | 3.40                       | 4.30                      | 3.82                      | 2.48                     | 3.33                   | 3.04                |
| Nitrogen.... | 6.16                     | 8.24                       | 10.96                     | 5.02                      | 2.50                     | 0.32                   | 0.08                |
| Oxygen.....  | 45.65                    | 34.14                      | 35.97                     | 40.14                     | 40.72                    | 47.07                  | 39.04               |
| Total.....   | 100.00                   | 100.00                     | 100.00                    | 100.00                    | 100.00                   | 100.00                 | 100.00              |
|              | Highest.<br>Per cent.    |                            | Lowest.<br>Per cent.      |                           | Difference.<br>Per cent. |                        |                     |
| Carbon.....  | 57.84 sugar.             |                            | 41.95 cow manure.         |                           | 15.89                    |                        |                     |
| Hydrogen.... | 6.26 cow manure.         |                            | 2.48 oat straw.           |                           | 3.78                     |                        |                     |
| Nitrogen.... | 10.96 meat scraps.       |                            | 0.08 sugar.               |                           | 10.88                    |                        |                     |
| Oxygen.....  | 47.07 sawdust.           |                            | 34.14 green clover.       |                           | 12.93                    |                        |                     |

The differences in composition are noticeable. The humus produced by each material, as meat scraps, green clover, or sawdust, is different from the humus produced by every other material. There is not a general similarity in composition between the humus produced by any two of the materials. The humus produced by sugar may be taken as a type of a non-nitrogenous humus. The small amount of nitrogen present in the sugar humus has been derived from the nitrogen present in the soil. The humus from meat scraps may be taken as a type of humus produced from a nitrogenous material. The nitrogen content of the humus ranges from about one-tenth per cent. in sugar humus to nearly eleven per cent. in the meat scraps humus. The humus from materials as meat scraps and green clover must be exceedingly complex, because each material is composed of both nitrogenous and non-nitrogenous compounds, and each class of compounds is capable of being

split up into still other compounds, each one having a different action in humification processes. It is evident that any formulas applied to the compounds, as a whole, would, to say the least, fail to express the composition of humus.

Although the proximate composition of humus as yet, can not be given, or formulas assigned to these compounds, the nature of the humus as nitrogenous or non-nitrogenous can be determined.

There appears to have been no classification of the humus compounds proposed since the classification of Mülder, in 1840, as follows:

|                | Ulmic and<br>ulmic acid.<br>Per cent. | Humin and<br>humic acid.<br>Per cent. | Crenic<br>acid.<br>Per cent. | Approcrenic<br>acid.<br>Per cent. |
|----------------|---------------------------------------|---------------------------------------|------------------------------|-----------------------------------|
| Carbon.....    | 67.1                                  | 64.4                                  | 44.0                         | 34.4                              |
| Hydrogen ..... | 4.2                                   | 4.3                                   | 5.5                          | 3.5                               |
| Nitrogen ..... | ...                                   | ...                                   | 3.9                          | 3.0                               |
| Oxygen .....   | 28.7                                  | 31.3                                  | 46.6                         | 39.1                              |
|                | 100.00                                | 100.00                                | 100.00                       | 100.00                            |

Corresponding to  $C_{40}H_{28}O_1 + H_2O$ ;  $C_{21}H_{24}O_{12} + 3H_2O$ ;  
 $C_{12}H_{12}O_6$  (?);  $C_{24}H_{24}O_{12}$  (?).

None of the humus materials produced in these culture experiments have the same composition as given above. The sawdust and sugar humus approach in composition nearest to the humic and ulmic compounds. The differences are, however, great.

It would seem best, in the present state of knowledge, to make the divisions on the basis of nitrogen, as :

- I. The non-nitrogenous humus group, as sugar humus.
- II. The nitrogenous group, divided into three or four sub-groups, as (1) humus containing one to two per cent. nitrogen, as sawdust humus; (2) humus containing two to four per cent. nitrogen, as oat straw humus; (3) humus containing four to eight per cent. nitrogen, as cow manure and clover humus; and (4) humus containing over eight or nine per cent. nitrogen, as meat scrap humus.

Such a division would give an approximate idea as to the nature of the materials from which the humus has been derived, as well as an approximate idea of its agricultural value. As ordinarily used, the term humus is a very indefinite one so far

as conveying any idea as to its chemical composition or probable value.

*Formation of Humates.*—The analysis of the ash from the precipitated humus compounds shows the presence of potassium, calcium, iron, aluminum, phosphorus, sulphur, and other elements. There is every indication that these elements are in organic combination with the carbon, hydrogen, nitrogen, and oxygen of the humus. When the alkaline humus solution is neutralized, the ash elements are precipitated with the humus materials. The mineral matter combined with the humus is different in composition and solubility from ordinary soil. The average composition of the ash from eight samples of precipitated humus was found to be as follows:

|                             | Percent. |
|-----------------------------|----------|
| Insoluble matter (HCl)..... | 61.97    |
| Potash .....                | 7.50     |
| Soda .....                  | 8.13     |
| Lime.....                   | 0.09     |
| Magnesia.....               | 0.36     |
| Alumina .....               | 3.48     |
| Ferric oxide.....           | 3.12     |
| Phosphorus pentoxide.....   | 12.37    |
| Sulphur trioxide .....      | 0.98     |
| Carbon dioxide.....         | 1.64     |

Is the mineral matter, combined with humus, derived entirely from the mineral matter originally present in the humus-forming material, or is a part of it derived from the soil by the chemical action of the humus? That is, does the humus combine with the mineral matter of the soil to form compounds known as humates? In order to obtain data upon this question, initial and final weights of the soil and humus-forming materials used in the humus production experiments reported, were made, and the total grams of humic phosphoric acid and potash, in both the original soil and humus material, as well as the final product of the humus, were calculated. In many cases there were decided gains, showing that some of the mineral matter of the soil had entered into chemical combination with the humus-forming materials. In the following table the figures given for the original soil and humus are for the amounts present in the soil in humic forms plus the total amount of mineral matter in the substance used:

|                                   | Humic phos-<br>phorus pentoxide.<br>Grams. | Humic<br>potash.<br>Grams. |
|-----------------------------------|--|----------------------------|
| Cow manure humus.                 |  |                            |
| Original soil and manure.....     | 1.17                                       | 1.06                       |
| Final humus product .....         | 1.62                                       | 1.27                       |
| Green clover humus.               |  |                            |
| Original soil and clover.....     | 3.21                                       | 5.26                       |
| Final humus product.....          | 3.74                                       | 4.93                       |
| Meat scraps humus.                |  |                            |
| Original soil and meat scraps ... | 1.07                                       | 0.25                       |
| Final humus product.....          | 1.18                                       | 0.36                       |
| Sawdust humus.                    |  |                            |
| Original soil and sawdust .....   | 0.85                                       | 0.67                       |
| Final humus product .....         | 0.78                                       | 0.70                       |
| Flour humus.                      |  |                            |
| Original soil and flour .....     | 0.60                                       | 0.32                       |
| Final humus product .....         | 0.71                                       | 0.48                       |
| Oat straw humus.                  |  |                            |
| Original soil and straw.....      | 1.02                                       | 2.42                       |
| Final humus product .....         | 1.03                                       | 2.41                       |

There appears to be a great difference in the power which various materials possess of entering into chemical combination with the mineral matter of the soil to form humates. Some of the nitrogenous compounds seem to have a greater power of combining than the non-nitrogenous compounds. There is also a great difference in soils: some combine with the humus materials more readily than others.

The ultimate composition of the humus from different types of soil shows as wide a range as in the case of the humus prepared from the culture experiments. The nitrogen content of the humus ranges from one to ten per cent. The following examples show a range from six to ten. No. 1 is a sample made up of equal parts of eight rich prairie soils. No. 2 is a soil that has been under cultivation for a number of years. Nos. 3 and 4 are different types of soil. No. 3 has never been under cultivation, while No. 4 is a similar soil which has been cultivated for about forty years to small grains.

|                | No. 1.<br>Per cent. | No. 2.<br>Per cent. | No. 3.<br>Per cent. | No. 4.<br>Per cent. |
|----------------|---------------------|---------------------|---------------------|---------------------|
| Carbon.....    | 45.12               | 48.16               | 44.12               | 50.10               |
| Hydrogen ..... | 3.67                | 5.40                | 6.00                | 4.80                |
| Nitrogen ..... | 10.37               | 9.12                | 8.12                | 6.54                |
| Oxygen .....   | 28.60               | 33.16               | 35.16               | 33.66               |
| Ash .....      | 12.24               | 4.16                | 6.60                | 4.90                |

The humus from soils Nos. 1 and 2 would belong to the fourth class, while Nos. 3 and 4 would belong to the third class of nitrogenous humus compounds. For reasons given it would be impossible to assign, from these analyses, any formulas to the humus. The next best thing that can be done is to assign to the humus its probable agricultural value, which can best be done on the basis of the nitrogen content of the humus. This would involve simply a determination of the humus, and also a determination of the nitrogen content of the humus. The following working directions for these two determinations have been found to work well with ordinary soils.

*Determination of Humus.*—Weigh out either five or ten grams of soil into a 200 cc. wide mouthed glass-stoppered bottle. If the soil is poor in organic matter, fifteen or twenty grams should be taken. Add 100 cc. of a one per cent. solution of hydrochloric acid. If the soil contains more than one per cent. lime, then a two per cent. solution of hydrochloric acid may be used. Place the stopper in the bottle and shake vigorously. After allowing the acid to act on the soil for five or ten hours the solution is decanted into a filter, a fresh quantity of 100 cc. of acid is added, it is decanted, and the contents of the bottle are transferred to the funnel. The soil, in the funnel, is then washed with the dilute acid until no reaction for lime is obtained, and then with distilled water until the washings are only slightly turbid with silver nitrate. After receiving the above treatment the soil is transferred from the funnel to the stoppered bottle, using 150 cc. of a three per cent. solution of ammonia. The bottle containing the soil and ammonia solution is occasionally shaken, and after five or six hours the solution is decanted into a 500 cc. measuring flask. A fresh quantity of about 100 cc. of ammonia is added to the soil in the bottle, and after acting on the soil for three or four hours it is decanted and added to the first extract. After the third extraction, the extract usually becomes nearly colorless. After the fourth extraction the humus solution in the flask is made up to 500 cc. and allowed to settle. If the soil contains a large amount of fine clay it will be necessary to allow from two to ten hours, or longer, for the soil particles to settle. A 50 or 100 cc. portion of the filtered humus extract is evaporated to dryness in a tared platinum dish. After

drying in an air-bath at  $101^{\circ}$  or  $102^{\circ}$  (on account of the tenacity with which the humus retains water), the dish with the humus materials is weighed, then ignited, and weighed again. The loss of weight is calculated as humus. The humus extract may be either black or brown.

*Nitrogen Content of the Humus.*—Either five or ten grams of soil are first treated with dilute hydrochloric acid, in the same way as in the humus determination. If the soil contains only a small amount of organic material, fifteen or twenty grams should be taken for this determination. After treatment with acid the soil is extracted with a three per cent. solution of sodium hydroxide in the same way as for the ammonia extraction. Two hundred cc. of the filtered solution are evaporated nearly to dryness in a Kjeldahl distillation flask, after first making the solution acid with sulphuric acid. The nitrogen determination is then completed in the usual way.

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## THE ACTION OF CERTAIN BODIES ON THE DIGESTIVE FERMENTS.

By FRANK D. SIMONS.

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VERY little attention seems to have been given to the study of the action of some of our common coloring matters, flavoring extracts, and preservatives on the digestive ferments. The object of my work, therefore, has been to test, from a physiological standpoint, the deportment of members of the above three classes of bodies towards digestion.

As far as my searches have extended, I have been able to find but very little literature bearing on this subject. Professor Chittenden, of the Sheffield Scientific School, has furnished many valuable contributions to our knowledge of digestion. He includes in a list of bodies antagonistic to the peptic ferment, potassium permanganate, borax, ammonia-alum, sodium salicylate, quinuine, and the salts of nearly all of the alkaloids.

Dr. H. A. Weber<sup>1</sup> investigated the behavior of three coal-tar coloring matters (*viz.*, oroline yellow, saffoline, and magenta) towards digestion. Although these bodies have been included in the list of harmless colors, yet he found that each one, even

<sup>1</sup>This Journal, 18, 1092, 1896.

when taken in a very minute quantity, arrested digestion, some of them that of the stomach, others that of the intestines, though in no case did he find that any one substance alone had a retarding effect on both peptic and pancreatic digestion. From his results then, it would seem that these substances are very harmful, inasmuch as they interfere seriously with the natural functions of the digestive organs, or more correctly speaking, with their secretions.

As an example of the possible danger from the indiscriminate use of these comparatively unknown (at least so far as concerns their relations toward digestion) colors, we quote the results of Mr. Weber's experiments with oroline yellow on stomachic digestion :

" This color was one of a series employed in the coloring of confectionery, and was found to be what is known in the trade as acid yellow or fast yellow, and is a mixture of sodium amidoazobenzenedisulphonate with sodium amidoazobenzenemonosulphonate.

|        | Amount<br>of color.<br>Gram. | Amount<br>of fibrin.<br>Gram. | Amount<br>of pepsin.<br>Gram. | Duration of<br>experiment.<br>Hours. | Amount of<br>fibrin dissolved.<br>Gram. |
|--------|------------------------------|-------------------------------|-------------------------------|--------------------------------------|---|
| I..... | 0.0                          | 1                             | 0.020                         | 3                                    | 1.00                                    |
| 2..... | 1.0                          | 1                             | 0.020                         | 3                                    | 0.10                                    |
| 3..... | 0.5                          | 1                             | 0.020                         | 3                                    | 0.12                                    |
| 4..... | 0.25                         | 1                             | 0.020                         | 3                                    | 0.22                                    |
| 5..... | 0.125                        | 1                             | 0.020                         | 3                                    | 0.35                                    |
| 6..... | 0.062                        | 1                             | 0.020                         | 3                                    | 0.73                                    |

From this it will be seen that even in test No. 6, where the color employed amounted to only one part in 1,600 parts of the solution, the presence of the color had still a depressing effect. On the whole it must be conceded that this color has a marked and injurious effect on peptic digestion."

Now when we see what a small portion of the poison (I call it so, for undoubtedly it is) will retard digestion, the only natural inference, which one might draw, would be that it is antagonistic to the normal action of the organs. However, that is a question for the physician rather than for the chemist, for while the latter performs the experiments, the former applies their results.

In carrying on an artificial process of digestion the substance usually employed to be digested is freshly prepared blood fibrin or purified and coagulated egg-albumin.

To prepare the former the blood fresh from the artery must be well whipped, and the fibrin thus obtained washed quickly and thoroughly with water. When washed well, it should be perfectly white, showing no tint of red. While the freshly prepared fibrin is always better for the tests, yet, as the investigator is seldom in a position where this can be accomplished without some difficulty and loss of time, it may be preserved to good advantage in alcohol; in this manner it can be kept from decomposition for some time. Before using, however, it must be washed entirely free from the spirits, then dried, and the amount of material desired weighed.

To prepare coagulated egg-albumin treat the whites of freshly laid eggs with an equal volume of water, shake well, and exactly neutralize with hydrochloric acid. Then filter until the filtrate is comparatively clear, and pour into about an equal volume of boiling water. Render faintly acid with acetic acid<sup>1</sup> and heat to vigorous boiling. The precipitate is now filtered off, and washed several times with boiling water. It is then ready for use, and like fibrin may be preserved to good advantage in alcohol. When the process has been rightly carried on, the albumin should be perfectly white, firm, and capable of being easily washed and dried. There should be no sticky feeling when held in the hands, and when such is the case, it must be submitted to further boiling, and perhaps even to a slight neutralization.

I found the albumin to be better for my experiments than the fibrin, as it is more delicate in reaction; that is, it is a little more difficult to digest than the fibrin, thus showing retarding effects to a finer degree. However, when the latter substance is employed in the process, the work must not be delayed; in other words, after digestion has continued the desired number of hours, the undissolved fibrin should be quickly filtered, washed, and weighed; for fibrin decomposes rather quickly in the air, and by that means some of the undissolved substance might be lost, which, of course, would lead to erroneous results.

As an artificial gastric juice the following proportion was used: Two-tenths gram of purified pepsin dissolved in 10.2 cc. hydrochloric acid (sp. gr. 1.14), and this then made up to a liter.

<sup>1</sup>Care must be taken to add only just enough of the reagent to render the liquid very faintly acid. It must be remembered that albumin is very soluble in a slight excess of the acid.

Gastric juice prepared by simple extraction from pigs' stomachs with hydrochloric acid is not only not constant, but also often faulty in its action. These extracts contain slime-like albuminous bodies (not further understood) which contaminate the digestion. In order to avoid this, Kühne<sup>1</sup> recommends a juice prepared in the following manner:

"The prepared mucous membrane of the pig's stomach is digested six days at 40° C. with seven times its quantity of a five-tenths per cent. hydrochloric acid solution. Saturate now directly with ammonium sulphate; collect the precipitate as completely as possible, and wash with water. Dissolve in digestion hydrochloric acid (five-tenths per cent.) five times the amount of the membrane taken, which contains (0.25 per cent.) thyme oil, and again digest one day at 40° C. Saturate now with ammonium sulphate. The residue ('purified pepsin') is used for the digestion by suspending it in digestion hydrochloric acid."

To avoid the difficulty and loss of time attending the preparation of pepsin, the powdered article from the laboratories of Armour & Co. is recommended. If this extract is used, the juice should be made up in the above proportion: *viz.*, two-tenths gram pepsin, and 10.2 cc. hydrochloric acid (sp. gr. 1.14) dissolved in one liter of water.

For the intestinal digestion the artificial pancreatic juice was made by dissolving a mixture of three grams pancreatine (procured of Armour & Co.) and fifteen grams sodium bicarbonate in one liter of water. The pancreatic solution may, however, be prepared in the following manner:

After removing the fat from the pancreas of a beef, divide that organ finely (with a sausage mill or chopping knife). Triturate with fine, clean sand, and let stand twenty-four to thirty-six hours at 14°. Now treat the mixture with glycerol and water, employing for every 400 grams pancreas one liter of glycerol (sp. gr. 1.23) and one liter of water. After the lapse of three days press in a filter press, then through filter paper, and to the filtrate add five cc. chloroform (to prevent bacterial changes). Preserve in a cool place. When used, one gram sodium bicarbonate is added to each 100 cc. of the trypsin solution.

<sup>1</sup> *Zeit. f. Biol.*, 29, 426-428.

In carrying on my experiments a control test, consisting of a mixture of 100 cc. of the digestive liquid and one gram of the substance to be digested (blood fibrin or egg-albumin), was placed in a 150 cc. flask, immersed in a water-bath, and subjected to a temperature of from 38° to 40° C., until complete digestion was manifest. Then, at the same time, and under the same conditions, similar mixtures, but with the addition of varying quantities of the body to be tested, were subjected to a like treatment. When the digestion of the control test was completed, all of the tests were cooled to the temperature of the laboratory, and then filtered and washed through tared filter papers. After drying, they were weighed, using the control filter paper as a control weight, and the amount of the undigested material thus calculated.

It can be seen from the method of procedure that my results are, to a certain extent, approximate. They are, however, accurate enough to show distinctively the behavior of the substances tested toward the digestive ferments.

I have grouped the substances with which I worked under the following heads, and this order will be adhered to in their discussion :

I. Digestion retarded even after prolonged treatment:

a. *Peptic*:

- Picric acid.
- Tropaeolin ooo.
- Metanil yellow.

b. *Pancreatic*:

- Bismark brown.
- Cinnamon.
- Formol.

II. Digestion ensues only after prolonged treatment:

*Peptic*:

- Salicylic acid.
- Oil of wintergreen.

III. Digestion progresses normally:

*Peptic and Pancreatic*:

- Essence of peppermint.
- Chrysoidine.
- Safranine.
- Methylene blue.

PICRIC ACID, C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>OH.

The following results were obtained:

## PEPTIC DIGESTION.

| Test. | Amount of substance.<br>Gram. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
|-------|-------------------------------|-----------------------------|-----------------------------------|---------------------------------|
| 1     | 0.00                          | 1                           | 6                                 | 0.00                            |
| 2     | 0.60                          | 1                           | 6                                 | 1.00                            |
| 3     | 0.30                          | 1                           | 6                                 | 0.92                            |
| 4     | 0.20                          | 1                           | 6                                 | 0.76                            |
| 5     | 0.10                          | 1                           | 6                                 | 0.55                            |
| 6     | 0.06                          | 1                           | 6                                 | 0.32                            |

## PANCREATIC DIGESTION.

|   |      |   |    |      |
|---|------|---|----|------|
| 1 | 0.00 | 1 | 12 | 0.00 |
| 2 | 0.60 | 1 | 12 | 0.00 |
| 3 | 0.30 | 1 | 12 | 0.00 |
| 4 | 0.20 | 1 | 12 | 0.00 |
| 5 | 0.10 | 1 | 12 | 0.00 |
| 6 | 0.06 | 1 | 12 | 0.00 |

From the above results it will be seen that while the acid had a distinctively depressing effect on the peptic ferment—as is shown even in test No. 6, where the amount of the acid was only one part in 1,666 parts of the solution—yet its deportment toward the pancreatic ferment was perfectly normal.

The presence or absence of digested albumin in the solution may be proved by the addition of a solution of tannin, which reagent precipitates albuminous bodies.

TROPAEOLIN OOO No. 1, NaSO<sub>4</sub>.C<sub>6</sub>H<sub>4</sub>.N : N.C<sub>6</sub>H<sub>5</sub>OH.

## PEPTIC DIGESTION.

| Test. | Amount of substance.<br>Gram. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
|-------|-------------------------------|-----------------------------|-----------------------------------|---------------------------------|
| 1     | 0.00                          | 1                           | 6                                 | 0.00                            |
| 2     | 0.60                          | 1                           | 6                                 | 1.00                            |
| 3     | 0.30                          | 1                           | 6                                 | 0.96                            |
| 4     | 0.20                          | 1                           | 6                                 | 0.84                            |
| 5     | 0.10                          | 1                           | 6                                 | 0.70                            |
| 6     | 0.06                          | 1                           | 6                                 | 0.48                            |

Thus it will be seen that this body has a very deleterious effect in the peptic ferment.

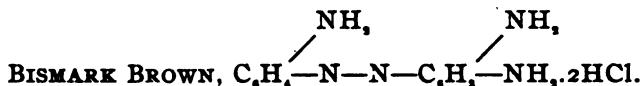
The color was found to have no retarding effect on the intestinal digestion, the albumin in all of the tests dissolving completely at the expiration of twelve hours.

METANIL YELLOW,  $\text{NaSO}_3\text{C}_6\text{H}_4\text{N} : \text{N.C}_6\text{H}_4\text{NH.C}_6\text{H}_4$ .

## PEPTIC DIGESTION.

| Test. | Amount of substance.<br>Gram. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Grams. |
|-------|-------------------------------|-----------------------------|-----------------------------------|----------------------------------|
| 1     | 0.00                          | I                           | 6                                 | 0.00                             |
| 2     | 0.60                          | I                           | 6                                 | 1.00                             |
| 3     | 0.30                          | I                           | 6                                 | 0.93                             |
| 4     | 0.20                          | I                           | 6                                 | 0.52                             |
| 5     | 0.10                          | I                           | 6                                 | 0.41                             |
| 6     | 0.06                          | I                           | 6                                 | 0.32                             |

This color, like the two preceding, has a markedly depressing effect on peptic ferment, but none at all on the pancreatic.



## PANCREATIC DIGESTION.

| Test. | Amount of substance.<br>Gram. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
|-------|-------------------------------|-----------------------------|-----------------------------------|---------------------------------|
| 1     | 0.00                          | I                           | 12                                | 0.00                            |
| 2     | 0.60                          | I                           | 12                                | 1.00                            |
| 3     | 0.30                          | I                           | 12                                | 0.88                            |
| 4     | 0.20                          | I                           | 12                                | 0.63                            |
| 5     | 0.10                          | I                           | 12                                | 0.50                            |
| 6     | 0.06                          | I                           | 12                                | 0.26                            |

This color neither prevented nor delayed the peptic digestion.

The addition of Bismark brown to the pancreatic juice produced a heavy precipitate, consisting of the free color base. Therefore, control tests had to be made for these experiments. This was done by subjecting the same amount of the color to treatment similar to that of the test then being made—but without the addition of the substance to be digested—and after filtration, by using this precipitate and filter paper as a control weight.

In order to show that the depressing action on the ferment was caused by the Bismark brown itself, rather than by any mechanical influence which might have been produced by the presence of the precipitate in the solution, another test was made, wherein the precipitate was filtered off before the addition of the albumin, and the clear filtrate used as the digestion fluid. The result of this experiment was that the action of the ferment

was interfered with to the same extent as in the tests in which the precipitate was present.

#### CINNAMON.

The spirit of essence of cinnamon, prescribed by the U. S. Pharmacopoeia, is made up in the following proportions: Ten parts (one oz. av.) oil of cinnamon, and ninety parts alcohol.

The essence, prepared as given above, was used in the following experiments:

#### PANCREATIC DIGESTION.

| Test. | Amount of substance.<br>Drops. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
|-------|--------------------------------|-----------------------------|-----------------------------------|---------------------------------|
| 1     | 00.0                           | 1                           | 12                                | 0.00                            |
| 2     | 30.0                           | 1                           | 12                                | 1.00                            |
| 3     | 20.0                           | 1                           | 12                                | 0.90                            |
| 4     | 10.0                           | 1                           | 12                                | 0.68                            |
| 5     | 5.0                            | 1                           | 12                                | 0.24                            |

No disturbance of the action of the peptic ferment by the introduction of this substance was produced, the digestion of the albumin in all of the experiments keeping pace with that of the control test.

#### FORMOL.<sup>1</sup>

A forty per cent. solution of formic aldehyde was used in these experiments.

#### PANCREATIC DIGESTION.

| Test. | Amount of substance.<br>Drops. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
|-------|--------------------------------|-----------------------------|-----------------------------------|---------------------------------|
| 1     | 00.0                           | 1                           | 12                                | 0.00                            |
| 2     | 35.0                           | 1                           | 12                                | 1.00                            |
| 3     | 25.0                           | 1                           | 12                                | 0.82                            |
| 4     | 15.0                           | 1                           | 12                                | 0.60                            |
| 5     | 10.0                           | 1                           | 12                                | 0.44                            |
| 6     | 5.0                            | 1                           | 12                                | 0.18                            |

As in the case of the two preceding substances, formol had no apparent effect on peptic digestion.

It is seen from the above tests that this preservative has a very depressing action on the pancreatic ferment, even one part in 2,000 parts of the solution (test No. 6) being sufficient to distinctively retard digestion.

<sup>1</sup> Formula (?)  $\text{C}(\text{H})_3(\text{OH})_2$ . Cf. *Chem. Ztg.*, 1890, 1408.

**SALICYLIC ACID, C<sub>6</sub>H<sub>4</sub>(OH).COOH.**

This body was found to retard the action of the peptic ferment, inasmuch as it considerably prolonged the time for complete digestion. Therefore, I made two series of tests: In the first, the amount of undissolved albumin at the completion of the digestion of the check test was recorded; in the second, the time necessary for complete digestion was noted. Thus:

| Test. | PEPTIC DIGESTION.             |                             |                                   |                                 |
|-------|-------------------------------|-----------------------------|-----------------------------------|---------------------------------|
|       | Amount of substance.<br>Gram. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
| 1     | 0.00                          | 1                           | 6                                 | 0.00                            |
| 2     | 0.60                          | 1                           | 6                                 | 0.85                            |
| 3     | 0.30                          | 1                           | 6                                 | 0.56                            |
| 4     | 0.20                          | 1                           | 6                                 | 0.34                            |
| 5     | 0.10                          | 1                           | 6                                 | 0.25                            |
| 6     | 0.06                          | 1                           | 6                                 | 0.10                            |
| 1     | 0.00                          | 1                           | 6                                 | 0.00                            |
| 2     | 0.20                          | 1                           | 11                                | 0.00                            |
| 3     | 0.10                          | 1                           | 9½                                | 0.00                            |
| 4     | 0.06                          | 1                           | 7                                 | 0.00                            |

This acid is generally conceded to have a retarding action on digestion;<sup>1</sup> my reason for experimenting with it, however, was that I wished to compare the results with those of the following substance, wintergreen, the active principle of which is methyl salicylate.

WINTERGREEN.

For the following tests I used a preparation procured at a pharmacy, and recommended as the natural oil of wintergreen.

As in my experiments with salicylic acid, I conducted here two series of tests—first, the amount of material undissolved at the completion of the digestion of the control test was recorded, and second, the time for complete digestion was noted.

| Test. | PEPTIC DIGESTION.              |                             |                                   |                                 |
|-------|--------------------------------|-----------------------------|-----------------------------------|---------------------------------|
|       | Amount of substance.<br>Drops. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
| 1     | 00.0                           | 1                           | 6                                 | 0.00                            |
| 2     | 30.0                           | 1                           | 6                                 | 0.74                            |
| 3     | 20.0                           | 1                           | 6                                 | 0.58                            |
| 4     | 15.0                           | 1                           | 6                                 | 0.42                            |
| 5     | 10.0                           | 1                           | 6                                 | 0.38                            |
| 6     | 5.0                            | 1                           | 6                                 | 0.16                            |

<sup>1</sup> Olaf Hammarsten: *Physiological Chemistry*, 1893.

| Test. | Amount of substance.<br>Drops. | Amount of albumin.<br>Gram. | Duration of experiment.<br>Hours. | Material not digested.<br>Gram. |
|-------|--------------------------------|-----------------------------|-----------------------------------|---------------------------------|
| 1     | 00.0                           | 1                           | 6                                 | 0.00                            |
| 2     | 15.0                           | 1                           | 12                                | 0.00                            |
| 3     | 10.0                           | 1                           | 11                                | 0.00                            |
| 4     | 5.0                            | 1                           | 8                                 | 0.00                            |

By comparing the results of the experiments of salicylic acid and wintergreen a striking similarity of action on the peptic ferment will be noticed.

Wintergreen, as was expected from the behavior of salicylic acid, had no influence on the pancreatic digestion.

#### PEPPERMINT.

The essence, prepared according to the U. S. Pharmacopeia, *viz.*, oil of peppermint one fluid ounce, rectified spirits four fluid ounces, was used in my experiments with this body.

The action of peppermint on both the peptic and pancreatic ferments was found to be practically *nūl*. For this reason it is useless to tabulate the different tests which were made. It is enough to say that the albumin in all cases, where the amount of the essence introduced varied from ten drops to three cc., digested in a perfectly normal manner; in other words, complete solution had taken place at the end of six hours for peptic and twelve hours for pancreatic.

The three coloring matters, chrysoidine, saffranine, and methylene blue, like the essence of peppermint, had no apparent effect on the action of either of the ferments. In all of the tests made, with the amount of the color introduced varying from 0.06 to 1.00 gram, the albumin was found to be completely dissolved at the end of the allotted time.

Summing up my experiments now, it will be seen that of the twelve substances with which I worked, three (picric acid, troaeolin ooo, and metanil yellow) distinctly arrested peptic digestion, three (Bismark brown, cinnamon, and formol) pancreatic digestion, two (salicylic acid and wintergreen) partially arrested peptic digestion, and four (peppermint, chrysoidine, saffranine, and methylene blue) had no apparent effect on either of the ferments.

It is probably assuming too much for one to assert, or to state as having proved, that certain bodies completely arrest digestion. This will be seen at once if we consider that these artificial processes of digestion probably differ in a great many respects from those natural processes occurring in the stomach and intestines.

An answer to the question, "Does a substance seriously arrest digestion?" is perhaps not, strictly speaking, to be given in general, because the results obtained hold good only for the conditions under which the experiments were conducted; in other words, the neutralization capacity of the products of digestion must be taken into consideration. However, if we can show that some substances by themselves entirely, or nearly so, neutralize the action of the digestive ferments, we must naturally, and justly too, I think, infer that they have a very decided unwholesome effect on some of nature's functions. For, even if we assume that as fast as one portion of the digestive fluid is neutralized more is supplied until the right proportion for normal digestion is reached, one must see what a drain these inimical substances cause the organs to be subjected to. The organs supplying the fluids must be subjected to double, triple, or perhaps even more, work than that which normally they are required to perform; and the food too remains in the stomach and intestines a much longer period of time than usual, which fact alone would prove the arresting power of these foreign bodies.

COLUMBIAN UNIVERSITY, WASHINGTON, D. C.

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[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN.]

## A PRELIMINARY THERMOCHEMICAL STUDY OF IRON AND STEEL.

BY E. D. CAMPBELL AND FIRMAN THOMPSON.

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ALTHOUGH much work has been done upon the relation between the ultimate chemical composition and the mechanical and magnetic properties of iron and steel, very little has been done in the way of studying the question from a thermochemical standpoint.

In 1875 Troost and Hautefeuille<sup>1</sup> determined the amount of

<sup>1</sup> *Compt. rend.*, 80, 964.

heat evolved by treating several samples of pure iron, steel, and cast iron, with moist mercuric chloride, and came to the conclusion that the chemical compounds of iron and carbon were endothermic, that is, formed with absorption of heat, although those of manganese and carbon were exothermic. Later, in 1885, Osmond,<sup>1</sup> working in Troost's laboratory, obtained by dissolving samples of soft, medium, and hard steel, as well as white iron in ammonium copper chloride, results that contradicted those previously obtained by Troost and Hautefeuille. Osmond does not attempt to reduce the results obtained to calories, but states them in the number of degrees that 500 cc. of a saturated solution of ammonium copper chloride would be raised by dissolving one and a half grams of the metal operated upon.

He does not state the composition of the three steels and one white iron, except the per cents. of carbon, which were 0.17, 0.54, 1.17, and 4.10, respectively.

The rise in temperature for the three steels and cast iron is given by Osmond, as follows :

| Metal. | Carbon. | Annealed. | Cold rolled. | Quenched. |
|--------|---------|-----------|--------------|-----------|
| 1      | 0.17    | 2.151     | 2.247        | ....      |
| 2      | 0.54    | 2.111     | 2.207        | 2.222     |
| 3      | 1.17    | 1.895     | 2.018        | 2.056     |
| 4      | 4.10    | 1.419     | ....         | 1.632     |

From the fact that as the carbon increases the heat of solution of the annealed metals decreases, Osmond concludes that the combination of iron and carbon is accompanied by evolution of heat, not as Troost previously stated, with absorption of heat.

In order to bring out more clearly the influence of cold rolling and of hard metal, Osmond tabulates the above results, using the heat of solution of the annealed meal in each case as unity. The table given is as follows :

| Metal. | Annealed. | Cold rolled. | Quenched. |
|--------|-----------|--------------|-----------|
| 1      | 1.000     | 1.045        | ....      |
| 2      | 1.000     | 1.045        | 1.052     |
| 3      | 1.000     | 1.065        | 1.084     |
| 4      | 1.000     | ....         | 1.150     |

Osmond says : " These results are conclusive ; in every case, quenching, like cold rolling, is characterized by an augmentation in heat, which increases with the carbon content. We

<sup>1</sup> *Compt. rend.*, 100, 1228.

believe then, that the already very probable existence of two isomeric varieties of iron,  $\alpha$  and  $\beta$ , may be considered as established.

"The crystallized, at least partially crystalline,  $\alpha$ -iron is obtained by raising to full red heat, followed by slow cooling (annealing); it is transformed into  $\beta$ -iron (which the structure of quenched steel warrants us in regarding as amorphous) either by a permanent deformation at low temperature, or by rapid cooling from a red heat, but only then in the presence of carbon or of some other bodies (manganese, tungsten) exerting the same influence upon the properties of steel."

In order to maintain the allotropic hypothesis above stated, we must assume the heat of solution of  $\alpha$ -iron to be less than that of  $\beta$ -iron, and yet although the difference in the heat of solution of the annealed and quenched specimens given increases with the increase in the per cent. of carbon, the absolute amount of heat evolved by the high carbon steel quenched, containing presumably all  $\beta$ -iron, is not so great as that of the low carbon annealed steel, presumably  $\alpha$ -iron.

It was to try to determine whether carbon alone was responsible for the variations in the heat of solution of steels subjected to different heat treatments, that we undertook the work described hereafter.

The calorimeter employed consisted of four concentric beakers, the first and second, and third and fourth being separated by felt packing, leaving a closed air space between the second and third. The beaker in which the solution was performed was supported on a light cork ring cemented to the bottom of the inner beaker of the calorimeter, and was prevented from upsetting or touching the sides of this latter by thin strips of cork cemented to the sides of the inner beaker. The cover of the inner beaker consisted of a layer of felt held between disks of vulcanized rubber. This cover fitted close inside the inner beaker of the calorimeter and was perforated for the admission of the thermometers and stirrer.

The thermometers had a range of  $10^{\circ}$  each and were graduated to fiftieths of a degree. The stirrer, which extended almost to the bottom of the beaker in which the solution was performed, consisted of a glass rod bent at its lower end so as to stir the

entire solution and provided with small pieces of rubber cemented to it in such a way that they would sweep the entire bottom of the beaker, thus stirring up particles of metal and hastening the solution. Without the use of this device it was found impossible to get complete and certain solution in a short time, while with its use the time did not usually exceed fifteen to twenty minutes.

The stirrer was actuated constantly during the work by a water motor, the belt from which passed through a small hole in the wall of the constant temperature room in which the experiments were performed. The solution of all the samples was made in a slightly acid solution of potassium copper chloride made by dissolving the following constituents.

|   | Grams.  |
|---|---------|
| CuCl <sub>2</sub> , 2H <sub>2</sub> O ..... | 368.24  |
| KCl.....                                    | 325.80  |
| HCl (41 per cent. HCl).....                 | 255.01  |
| H <sub>2</sub> O.....                       | 1995.26 |

The constituents were accurately weighed out in each case on a large balance having a capacity of five kilos, and sensitive with this load to five milligrams, so that all solutions used throughout the work were practically identical.

The stock solution, after making, was allowed to stand over night, and was then filtered through asbestos and kept in a constant temperature room until ready for use. The mean specific heat of this solution was calculated from the weight of the constituents, using the following specific heats: Water 1, copper 0.095, potassium 0.164, chloride 0.1221, hydrogen in hydrochloric acid 3.41.

The mean specific heat of this stock solution, using these constants, was 0.748. The water equivalent of the beaker in which the solution was effected, of the immersed portion of the stirring rod, and the thermometer bulbs, was calculated from the weight of these, using 0.177 and 0.033 as specific heats of glass and mercury respectively. Although there may be a slight absolute error in the reduction of the temperatures observed to calories, owing to the specific heats used, since the same solution and apparatus were used throughout the work, the results were strictly comparable one with another, and the

absolute values are probably not more than one or two per cent. above or below those recorded.

The method of making the determinations was to put in the weighed beaker a weighed amount, usually about 275 grams of potassium copper chloride. The beaker was then placed in the calorimeter, with the cover on, and allowed to come to constant temperature. Since the stock solution was always kept in the constant temperature room the beaker containing the solution did not have to stand in the calorimeter more than about half an hour before the sample of steel could be added.

The sample of iron or steel was prepared by filing, or pounding the metal when too hard to file, but in all cases was reduced to a powder, fine enough to pass through a sieve with seventy meshes to the inch. This fine subdivision was necessary in order to insure rapid solution. When the temperature of the calorimeter had become constant two grams of the finely divided iron or steel were introduced into the beaker, the cover being temporarily raised for this purpose, and the stirrer was started. Solution was rapid, the maximum temperature in almost all cases being attained within fifteen to twenty minutes. The usual rise was from  $5^{\circ}$  to  $7^{\circ}$ . In one case, when the time of solution was unusually prolonged, about forty minutes being required, an allowance was made for loss by radiation. With temperature of the beaker  $6^{\circ}$  above that of the initial temperature, this loss was found to be  $0.24^{\circ}$  per hour. This correction had to be made only in one case.

The method of subjecting the different steels to heat treatment was as follows: Steel to be annealed was placed as far as possible out of access of air and heated to a temperature of between  $900^{\circ}$  and  $1,000^{\circ}$  and cooled very slowly. Quenched or hardened specimens were prepared from pieces of the annealed metal. Pieces of the steel usually weighing from 50 to 100 grams were placed in a porcelain tube having an internal diameter of about twenty mm. This tube was wrapped with two layers of asbestos paper and slipped inside an iron tube which extended about thirty cm. beyond the end of the porcelain tube.

The center of the iron tube, the portion containing the specimen to be heated, passed through a Hoskins gasoline furnace in such a way that the tube for a distance of from fifteen to eighteen

cm. could be easily raised to any desired temperature up to 1,200° C. Through the porcelain tube was introduced the thermal couple of a Le Chatelier pyrometer, the thermal junction being in direct contact with the piece of steel under treatment. The pyrometer had been carefully graduated and we think the temperatures given are accurate within probably 5° or less. The other end of the iron tube was kept closed during the heating by a cork in order to avoid oxidation. When everything was ready the temperature of the tube was slowly raised, the time usually being from twenty to forty minutes until the pyrometer indicated that the bar was at the desired temperature. When this was attained the cork was removed from the end of the tube and by quickly tilting the latter the piece of steel was dropped into ice-water at a temperature of from 4° to 5°. After the operation corrections for the temperature of the galvanometer, etc., was made, and the actual temperature at the moment of tilting the tube was calculated.

The heat of solution of the various samples of steel is shown in the following tables, Table I showing the influence of composition and varying heat treatment on the heat of solution, Table II showing heat of solution of other samples. The numbers given in the tables are the averages of at least two duplicates; the difference between two determinations on the same sample seldom exceeded four calories and only in one case was it six :

TABLE I.  
SHOWING INFLUENCE OF CHEMICAL COMPOSITION AND HEAT TREATMENT ON THE HEAT OF SOLUTION.

| Experiment No. | Name of metal. | Chemical composition. |       |       | Heat treatment. | Calories evolved per gram of<br>Fe + Mn. |
|----------------|----------------|-----------------------|-------|-------|-----------------|--|
|                |                | C.                    | Mn.   | P.    |                 |  |
| 1              | Pure iron wire | 0.018                 | none  | 0.050 | 0.023           | 659.6                                    |
| 2              | Car. H         | 0.09                  | 0.22  | 0.016 | annealed        | 659.1                                    |
| 3              | " "            | 0.09                  | 0.22  | 0.016 | "               | 637.0                                    |
| 4              | " "            | 0.09                  | 0.22  | 0.016 | "               | 714°                                     |
| 5              | " "            | 0.09                  | 0.22  | 0.016 | "               | 825°                                     |
| 6              | " "            | 0.09                  | 0.22  | 0.016 | "               | 925°                                     |
| 7              | " "            | 0.09                  | 0.22  | 0.016 | annealed        | 684.7                                    |
| 8              | Cl. 5          | 0.10                  | 0.484 | 0.119 | "               | Outside of bar.                          |
| 9              | " 5            | 0.10                  | 0.484 | 0.119 | "               | 1025°                                    |
| 10             | " 5            | 0.10                  | 0.484 | 0.119 | "               | 712.3                                    |
| 11             | " 5            | 0.10                  | 0.484 | 0.119 | "               | Inside of bar.                           |
| 12             | " 5            | 0.10                  | 0.484 | 0.119 | "               | 1025°                                    |
| 13             | N. S. 5        | 0.37                  | 0.820 | 0.160 | "               | 703.9                                    |
| 14             | " 5            | 0.37                  | 0.820 | 0.160 | "               | 632.9                                    |
| 15             | " 5            | 0.37                  | 0.820 | 0.160 | "               | 651.2                                    |
| 16             | " 5            | 0.37                  | 0.820 | 0.160 | "               | 676.0                                    |
| 17             | " 5            | 0.37                  | 0.820 | 0.160 | "               | 928°                                     |
| 18             | Car. I         | 1.22                  | 0.780 | 0.098 | annealed        | 707.6                                    |
| 19             | " "            | 1.22                  | 0.780 | 0.098 | "               | 1028°                                    |
| 20             | " "            | 1.22                  | 0.780 | 0.098 | "               | 741.1                                    |
| 21             | " "            | 1.22                  | 0.780 | 0.098 | "               | 587.3                                    |
| 22             | " "            | 1.22                  | 0.780 | 0.098 | "               | 728°                                     |
| 23             | " "            | 1.22                  | 0.780 | 0.098 | "               | 626.3                                    |
| 24             | T. S. D.       | 1.28                  | 0.330 | 0.018 | annealed        | 827°                                     |
| 25             | " "            | 1.28                  | 0.330 | 0.018 | "               | 653.2                                    |

TABLE II.  
HEATS OF SOLUTION OF OTHER SAMPLES.

| Experiment No. | Name of metal.        | C.     | Mn.   | P.    | S.    | Sl.   | Heat treatment.                      | Calories evolved per gram of Fe + Mn. |
|----------------|-----------------------|--------|-------|-------|-------|-------|--------------------------------------|---------------------------------------|
| 27             | C. R. M. Co. 5        | 0.36   | 1.25  | 0.122 | 0.128 | 0.046 | Normal.                              | 560.7                                 |
| 28             | Car. H.               | 0.55   | 0.70  | 0.027 | 0.026 | ...   | Annealed.                            | 562.0                                 |
| 29             | " "                   | 0.55   | 0.70  | 0.027 | 0.026 | ...   | Harden and reheated to 275°.         | 639.4                                 |
| 30             | Cast steel            | 0.76   | 0.27  | 0.017 | trace | 0.234 | Annealed.                            | 583.1                                 |
| 31             | No. 5. Char. pig iron | c 1.70 | trace | 0.260 | ...   | 0.262 | Normal.                              | 620.0                                 |
| 32             | Pure carbide of iron  | g 1.95 | none  | 0.026 | ...   | ...   | Annealed.                            | 647.3                                 |
| 33             | Swed. bar iron        | 6.64   | ...   | ...   | ...   | ...   | Normal.                              | 670.0                                 |
| 34             | Special iron          | 3.22   | 0.33  | 0.018 | 0.006 | ...   | Poured while molten into cold water. | 756.0                                 |
| 35             | " "                   | 3.±    | 0.33  | 0.944 | 0.006 | ...   | Poured while molten into cold water. | 798.0                                 |
| 36             | Pure Cu. wire         | ...    | ...   | ...   | ...   | ...   | Normal.                              | 60.2                                  |
| 37             | " "                   | ...    | ...   | ...   | ...   | ...   | Cooled slowly from 1,000°.           | 66.3                                  |
| 38             | " "                   | ...    | ...   | ...   | ...   | ...   | Quenched from 940°.                  | 58.2                                  |

The following points seem to be indicated by the results in Tables I and II.

*First.* In annealed metal, owing to the heat of formation of compounds of iron with carbon, the heat of solution diminishes as the per cent. of carbon increases, until after the saturation point (eight-tenths to nine-tenths per cent.) is passed, when, owing probably to the endothermic formation of non-crystalline cementite, the heat of solution increases again, but never reaches that of pure iron. This is shown in experiments 1, 2, 30, 24, 31.

The heat of solution of the last mentioned may be somewhat lowered by the presence of phosphorus and silicon, the decomposition of whose compounds would almost certainly absorb some heat.

*Second.* The presence of manganese, when combined with carbon in annealed metal, diminishes very markedly the heat of solution, owing to the greater stability of the compounds of manganese and carbon, compared with that of the corresponding compounds of iron. If there is not sufficient carbon to combine with the manganese, or if the carbon is above the saturation point, the substitution of manganese for iron seems to increase the heat of solution slightly, owing to the higher heat of formation of manganese chloride compared with that of ferrous chloride. This influence of manganese on heat of solution of annealed metal is clearly shown in experiments Nos. 2 and 8, 13 and 27; 28, 24, and 18.

*Third.* In the quenched metal, manganese seems to behave exactly the reverse from that in the annealed steel, the effect being to very notably increase the heat of solution, the increase being more marked the higher the temperature from which the steel is quenched. This is shown on comparing the heats of solutions of experiments Nos. 7 and 12, 17, 23 and 25.

*Fourth.* That phosphorus plays a considerable part in determining the heat of solution is shown by experiments 34 and 35, although these cannot be easily compared with the above, since the temperature from which the metal was quenched is not known, but must have been not far from 1,100° or 1,200°, as the metal was perfectly fluid when poured into cold water.

*Fifth.* The results obtained on copper (experiments 36, 37,

and 38) confirm those of Osmond, that is, that heat treatment has but slight influence on the heat of solution.

The next series of experiments undertaken was to determine the influence of reheating or "tempering" hardened steel upon its heat of solution. The steel selected for this purpose was the steel marked T. S. D. (see experiment 24, Table I). The steel had been hardened by heating to between 900° and 1,000° and quenching in ice-water. On account of the low phosphorus present in the metal we knew that it would be useless to attempt to get such steel as this in a sufficiently fine state of division for the work, if the metal was tempered before subdividing. High-grade tool steel of this class, if hardened and tempered, would be too hard to file and too tough to pulverize in a steel mortar, so that we resorted to the plan of pulverizing a considerable amount of the hardened metal and reheated the powdered steel in a stream of hydrogen or of nitrogen in order to avoid oxidation. For reheating to temperatures up to and including 400° from five to six grams of the bright powdered steel was placed in a large test-tube provided with a three-hole stopper; through one hole there was a tube for the purpose of conducting pure dry hydrogen nearly to the bottom of the test-tube; through the second hole a nitrogen filled thermometer was introduced, the bulb of the thermometer reaching to the bottom of the test-tube and being surrounded by the steel; the third hole was provided with a piece of tubing drawn down to a fine point, serving as an escape for the hydrogen.

For heating to 100° C. the test-tube so arranged was kept in a water-bath for twenty-four hours, the air in the test-tube having been displaced by pure dry hydrogen. For raising the temperature to from 200° to 400°, inclusive, the following device was employed: A piece of pig iron weighing about five kilos was drilled nearly through, the hole being somewhat larger than the diameter of the test-tube used. A little sand was placed in the hole, then the test-tube inserted deep enough so that the steel was a little below the center of the bar; the space around the test-tube was then filled with sand. This arrangement secured the slow, even heating of the sample. When the air in the test-tube had been completely displaced by dry hydrogen, the bar was slowly heated until the thermometer indicated the desired

temperature. The light was then turned out and the tube allowed to cool in hydrogen. For temperatures higher than 400° the powdered steel was placed in a porcelain combustion boat contained in a porcelain combustion tube. One end of this latter was closed by a one-hole stopper through which the dry hydrogen or nitrogen employed was conducted. In the other end of the combustion tube the thermal couple of the pyrometer was introduced in such a way that the thermal junction rested on the boat containing the steel. The portion of the tube containing the boat was then slowly heated in an ordinary combustion furnace, or for higher temperatures in a gasoline furnace, until the desired temperature was attained, then allowed to cool, the current of hydrogen or nitrogen being kept up during the cooling. Bright powdered steel underwent no apparent change in color, only when heated to 1,024° the mass showed a slight tendency to stick together.

In addition to determining the heat of solution of these reheated samples, we made colorimetric carbon determinations, using the annealed steel carbon, 1.28 per cent., as a standard.

The results of the reheating on the heat of solution and the color carbon determinations are embodied in Table III.

TABLE III.

## SHOWING INFLUENCE OF TEMPERING ON HEAT OF SOLUTION AND COLOR CARBON TEST.

| Experi-<br>ment No. | Temperature to<br>which metal<br>was raised. | Gas used. | Calories evolved<br>per gram<br>Fe + Mn. | Carbon<br>indicated<br>by color. |
|---------------------|--|-----------|--|----------------------------------|
| 39                  | 0  |           | 688.0                                    | 1.14                             |
| 40                  | 100°   | Hydrogen  | 685.8                                    | 1.14                             |
| 41                  | 200°   | "         | 685.8                                    | 1.14                             |
| 42                  | 250°   | "         | 673.9                                    | 1.14                             |
| 43                  | 300°   | "         | 666.0                                    | 1.18                             |
| 44                  | 400°   | "         | 662.5                                    | 1.20                             |
| 45                  | 500°   | "         | 657.6                                    | 1.27                             |
| 46                  | 600°   | "         | 634.7                                    | 1.27                             |
| 47                  | 715°   | "         | 631.8                                    | 1.16                             |
| 48                  | 750°   | "         | 687.4                                    | 1.03                             |
| 49                  | 1024°  | "         | 705.6                                    | 0.29                             |
| 50                  | 1024°  | Nitrogen  | 583.3                                    | 0.57                             |
| 51                  | 1024°  | "         | 560.6                                    | 0.73                             |

It will be noticed in this table that the heat of solution decreases and the apparent per cent. of carbon increases with

the temperature to which the metal is reheated until the critical point  $A_c$ , is passed. When the critical point  $A_c$ , is passed the hydrogen seems to combine with the carbon and the heat of solution rises very markedly. When the gas used was nitrogen, the temperature being over  $1,000^{\circ}$ , the nitrogen removes the carbon, part at least forming cyanogen, as was shown by passing the nitrogen through potassium hydroxide and precipitating silver cyanide with silver nitrate, after acidification with nitric acid. The heat of solution of the metal heated and cooled in nitrogen is very much lowered, being in fact what we might expect of ordinary annealed metal of the indicated per cent. of carbon, as brought out in Table I.

Why iron heated to high heats in hydrogen and cooled in this gas should increase the heat of solution, we are not at present prepared to state, but we hope to investigate this point in the near future.

The last set of experiments was made to show the influence of cold working upon the heat of solution and tensile strength of pure iron. The sample used was one of very fine No. 36 pure, bright iron wire twenty-two hundredths mm. in diameter and of the composition shown in experiment No. 1. In subjecting this to heat treatment small coils of the wire were placed in a porcelain combustion tube and slowly raised to the temperature indicated, as shown by the Le Chatelier pyrometer, a current of dry hydrogen being kept up during the operation.

As in the work on reheating powdered steel the metal was cooled in a current of hydrogen, after being heated to the desired temperature. After the heat treatment a portion of the metal was used for making tensile strength determinations and part was dissolved for determining the heat of solution. The results of this work are given in Table IV.

TABLE IV.

## SHOWING EFFECT OF REHEATING ON HEAT OF SOLUTION AND TENSILE STRENGTH OF COLD DRAWN IRON WIRE.

| Experi-<br>ment. No. | Temperature to<br>which wire<br>was raised. | Calories evolved<br>per gram of<br>Fe + Mn. | Tensile strength.<br>Kilos per<br>square mm. | Pounds per<br>square inch. |
|----------------------|---|---|--|----------------------------|
| 52                   | 0   | 802.1                                       | 96.8   | 135,520                    |
| 53                   | $400^{\circ}$                               | 750.6                                       | 74.2   | 103,880                    |
| 54                   | $609^{\circ}$                               | 663.9                                       | 42.1   | 58,940                     |
| 55                   | $765^{\circ}$                               | 659.6                                       | ....   | ....                       |

The following interesting relation is brought out in the above table. The diminution in tensile strength is almost exactly proportional to the diminution in the heat of solution. Thus, in reheating to 600° the heat of solution has fallen from 802.1 to 663.9, or 138.2 calories, while the tensile strength has fallen from 96.8 to 42.1, or 54.7 kilos per square mm., or the tensile strength has been reduced at the rate of 0.395 kilos per square mm. for each calorie diminution in the heat of solution. That this holds very nearly, is shown by the results obtained by reheating to 400°. The heat of solution has diminished 51.5 calories, which, if the tensile strength diminishes proportional to the falling off in the heat of solution, would indicate a tensile strength of 76.46 kilos, whereas the actual results gave 74.2 kilos.

If the increase in tensile strength accompanied by increase in heat of solution of this wire is due to allotropy in the iron induced by cold working, then the hardening of steel cannot easily be attributed to the same allotropic change, since the drawn iron wire has a higher heat of solution and hence presumably a higher proportion of non- $\alpha$ -iron than any of the hardened steels, and yet the wire is comparatively very soft, while many of the steels are hard enough to scratch glass easily.

Although a number of interesting facts have been brought out in the above work, the data obtained are yet too few to enable reliable conclusions to be drawn in regard to phenomena complicated by so many factors as are present in the work under examination.

We hope to continue the work along the lines indicated in the present paper and to obtain results more satisfactory than those herein described.

ANN ARBOR, MICH., June 24, 1897.

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#### NOTE.

The Fifteenth Annual Report of the Committee on Indexing Chemical Literature, just received from the chairman, Dr. Bolton, shows very great progress. Dr. Bolton's pioneer work has borne good fruit. Most books on chemistry now issued make some attempt at a bibliographic account of the subject-matter greatly to the benefit and convenience of the reader. Copies of the report may be obtained of the chairman, Dr. H. Carrington Bolton, Cosmos Club, Washington, D. C.

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**OBITUARY.**

PROF. EDGAR MCCLURE, professor of chemistry in the University of Oregon, Eugene, Ore., met his death on the ice slopes of Mt. Rainier, in the State of Washington, on the 27th day of July last. He was engaged at the time in the descent of the mountain, after having successfully made the ascent, and taken all the necessary measurements to determine the height of the mountain. When near the foot of the snowfield, night came on, and in the uncertain light his footing gave way, and he lost his life upon the rocks below.

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**NEW BOOKS.**

**THE PHASE RULE.** By W. D. BANCROFT. Large octavo. viii + 255. Ithaca, N. Y.: The Journal of Physical Chemistry. 1897. Price \$3.00.

In this book an attempt is made "to present the subject of qualitative equilibrium from the point of view of the Phase Rule and of the Theorem of Le Chatelier, without the use of mathematics." Such facts as bear upon the states and changes of equilibrium of a system of bodies; as determined by the temperature, pressure, and concentrations of its components, are here brought together and discussed in a methodical manner. Generally speaking, this has been admirably done, and the book should be of interest to chemists of every persuasion.

In an introductory chapter, the author defines and illustrates "phase" and "component," and states and explains Gibbs' Phase Rule and Le Chatelier's Theorem. He then passes to the consideration of a system consisting of one component; here the treatment of such familiar notions as boiling-point, sublimation, etc., will prove a revelation to many. Most of the book is devoted to systems containing two and three components, as the greater part of the experimental work on this subject has been confined to such systems. The concluding chapter gives the general theory of systems made up of four components, together with a *critique* of the meager experimental data pertaining to them.

The book has an especial value in that the author points out here and there in his theoretical discussions where further experimental work ought to be done, and, as has often been said,

the proposing of a good subject for research is often as difficult and as valuable as its experimental prosecution.

Also worthy of mention and commendation is the sharpness of definition of certain terms too commonly used in rather a loose sense. To be fair, however, it must be added that the author does not always show a just and impartial appreciation of experimental facts; if he can't give data a clear explanation in the light of his theory, then, he too often concludes, the data themselves must be in error. This is done, in one case, at least, where the author has not fully grasped the experimental facts.

The book, in places, is rather tedious reading, principally for this reason. The author often enters into the minutest details right in connection with general discussions and conclusions, which is somewhat bewildering and confusing. This might have been avoided, perhaps, by a more liberal use of foot-notes. There are also certain notions original with the author and occupying rather a prominent position throughout the work that do not seem to require so much emphasis, especially as they have not been adopted generally; thus the distinction between solvent and "solute," between "fusion" and "solubility" curves is hardly scientific or necessary.

Although the suppression of mathematics in the book may make it more acceptable to those chemists who are lacking in mathematical training, yet a certain amount of mathematical treatment of some points would have rendered them more intelligible as well as more in keeping with the historical development of the subject.

C. E. LINEBARGER.

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#### BOOKS RECEIVED.

An Electrolytic Method of Determining the Temperature of Soils. By Milton Whitney and Lyman J. Briggs. Bulletin No. 7, Division of Soils, U. S. Department of Agriculture, Washington, D. C. 15 pp.

An Electrolytic Method of Determining the Soluble Salt Content of Soils, with Some Results of Investigations on the Effect of Water and Soluble Salts on the Electrical Resistance of Soils. By Milton Whitney and Thos. H. Means. Bulletin No. 8. Division of Soils, U. S. Department of Agriculture, Washington, D. C. 30 pp.

Bulletin of the United States Geological Survey, No. 148. By F. W. Clarke and W. F. Hillebrand. U. S. Geological Survey, Washington, D. C. 306 pp. A Discussion of Methods of Analysis; Analyses of Various Rocks, Igneous and Crystalline, Stony Meteorites, Meteoric Iron, Sandstones and Cherts, Carbonate Rocks, Slates and Shales, Clays, Soils, etc., arranged and tabulated by F. W. Clarke.

Fertilizer Analyses of the Fertilizer Control. Special Bulletin No. 47. The North Carolina Agricultural Experiment Station, Raleigh, N. C., June 26, 1897. 8 pp.

Field Experiments with Sugar Cane. Seasons of 1893, 1894, and 1895. By Hubert Edson. Bulletin No. 12. Calumet Plantation, Patterson, La. 59 pp.

Ninth Biennial Report of the Director of the North Carolina Experiment Station, for the Two Years ending January, 1897. H. B. Battle, Director, Raleigh, N. C. 157 pp.

Sixth Annual Report of the Bureau of Labor, Statistics, and Mines, to the Governor and Fiftieth General Assembly of the State of Tennessee. 1896. A. H. Wood, Commissioner of Labor and Inspector of Mines, Nashville, Tennessee. 318 pp.

Geological Survey of Canada. G. W. Dawson, Director. Annual Report (New Series) with numerous maps. Vol. viii. 1895. Ottawa, Canada. xii + 154A + 120D + 184J + 387L + 59R + 103S pp. Price (with maps) \$1.00.

The Cost of Plant Food in Connecticut, Spring Months of 1897. Bulletin No. 124. Connecticut Agricultural Experiment Station, New Haven, Conn. June, 1897. 11 pp.

The Elements of Electro-Chemistry Treated Experimentally. By Dr. Robert Lüpke. Translated from the second revised and enlarged edition by M. M. Pattison Muir. London: H. Grevel & Co. Philadelphia: J. B. Lippincott Co. 1897. xv + 223 pp. 54 figures in the text. Price \$2.50.

The Composition of Prepared Cereal Foods. By E. E. Slosson. Bulletin No. 33. June, 1897. 14 pp. Wyoming Experiment Station, Laramie, Wyoming.

Incompatibilities in Prescriptions. For Students in Pharmacy and Medicine and Practicing Pharmacists and Physicians. By Edsel A. Ruddiman, Ph.D., M.D. 8vo., cloth. v + 264 pp. 1897. New York: John Wiley & Sons. Price \$2.00.

Ninth Annual Report of the Texas Agricultural Experiment Station for the Calendar Year 1896. Agricultural and Mechanical College of Texas, College Station, Brazos Co., Texas. 12 pp.

Steer Feeding. Bulletin No. 41. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas. 34 pp.

**Elements of Chemistry.** By Rufus P. Williams. viii + 412 pp. Boston: Ginn & Co. 1897. Price \$1.20.

**Water and Public Health. The Relative Purity of Waters from Different Sources.** By James H. Fuertes. x + 75 pp. 1897. New York: John Wiley & Sons. Price \$1.50.

**Exercises in Practical Physiology.** By Augustus D. Waller. Part III. **Physiology of the Nervous System. Electro-Physiology.** 91 pp. 1897. New York: Longmans, Green & Co. Price 90 cents.

## THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

## NOTES ON SELENIUM AND TELLURIUM.

BY EDWARD KELLER.

Received July 30, 1897.

IT is not very frequently that the technical chemist and the assayer, or the metallurgist, meet with the two elements, selenium and tellurium, although the assayer's work in gold assaying and treatment of the ores is often rendered more difficult by their presence. No analysis of any of the western, crude copper, however, is now complete without the joint, or separate, determination of selenium and tellurium.

It is not the object of this paper to fully describe any of the methods in use for their separation from other elements. A few new features, merely, will be pointed out.

It has long been known that many acid-forming elements are precipitated by ferric hydroxide as insoluble salts, from ammoniacal solution.

To have introduced this principle into copper analysis is entirely the merit of present and former chemists of the Baltimore Copper Smelting and Rolling Co.—the Messrs. Lehmann, Mager, and Johns.<sup>1</sup>

The elements of this group which occur, or may occur, in copper are phosphorus, arsenic, antimony, tin, selenium, and tellurium.<sup>2</sup> With all these elements this method may be most successfully employed when they are present in small quantity and the precipitation of the copper becomes impracticable.

<sup>1</sup> Lehmann and Mager: *Am. Chem. J.*, July, 1885.

<sup>2</sup> Cabell Whitehead: This Journal, 17, 280.

When the proper conditions are observed it is most efficient, rapid, and simple. From five to many hundred grams of copper, with a comparatively very small amount of iron, are dissolved in nitric acid, enough ammonia added to hold all copper in solution, boiled, and the ferric hydroxide filtered and washed.

From this precipitate the enumerated elements can easily be separated by known methods.

The following is illustrative of the behavior of selenium and tellurium in relation to this ferric hydroxide separation method. Of each element one gram was taken, and by oxidation with dilute nitric acid a solution of selenous and one of tellurous acid obtained. One gram of ferrous sulphate was dissolved and oxidized, and that amount of iron added to each solution, as well as to each succeeding filtrate (previously acidified) after the ferric hydroxide, precipitated by ammonia, was collected on a filter and washed. The ferric hydroxide precipitates were each dissolved in hydrochloric acid of the proper strength, and the selenium precipitated with ferrous sulphate, the tellurium with sulphur dioxide, and determined on tared filters.

The quantitative results were as follows:

| Element. | Quantity<br>Taken. | No. of precipitations. |        |        |        |        |        |        |        |        |       | Quantity<br>Found. |
|----------|--------------------|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------------------|
|          |                    | 1.                     | 2.     | 3.     | 4.     | 5.     | 6.     | 7.     | 8.     | 9.     | 10.   |                    |
| Gram.    | Gram.              | Gram.                  | Gram.  | Gram.  | Gram.  | Gram.  | Gram.  | Gram.  | Gram.  | Gram.  | Gram. | Gram.              |
| Se..     | 1                  | 0.0892                 | 0.0973 | 0.1546 | 0.1297 | 0.2219 | 0.1416 | 0.1236 | 0.0513 | 0.0121 | 0     | 1.0213             |
| Te..     | 1                  | 0.9548                 | 0.0448 | 0      | ....   | ....   | ....   | ....   | ....   | ....   | ....  | 0.9996             |

It is clear that the reaction is quantitative only when a certain excess of iron is present, which for selenium must be many times greater than for tellurium.

The method universally recommended for the separation of selenium and tellurium is the potassium cyanide method, selenium being readily soluble in a solution of that compound. Tellurium is also dissolved in small quantities, which must be again separated, and for that reason the method is unsatisfactory.

The best precipitant for both elements is declared to be sulphur dioxide.

To obtain the metallic precipitates by any reducing agents the two elements must be in solution as selenous and tellurous acids. The same is true if the sulphides are desired by precipi-

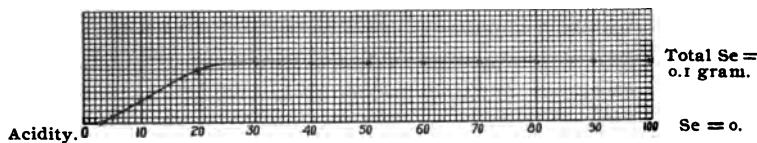
tation with hydrogen sulphide. Selenic and telluric acids are only reduced to the lower form by strong boiling hydrochloric acid. In describing the experiments made, the solutions spoken of are always those of the former acids.

In the reaction of selenous and tellurous acids with sulphur dioxide the two show characteristic differences. When precipitated by that gas no heavy metals must be present, since they are also, at least partially, precipitated.

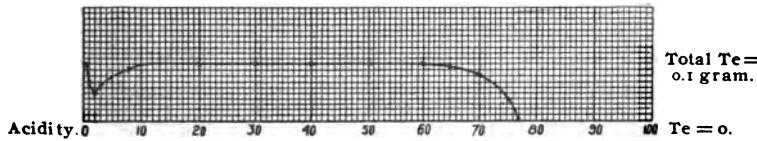
*Example.*—With one-half gram of copper and 0.1726 gram of selenium in solution, 0.0865 gram of copper was thrown down.

In the following determinations, the acid of which the percentage is given is strong hydrochloric of the specific gravity 1.175. The amount of selenium and tellurium in each case is

#### PRECIPITATION OF SELENIUM BY SULPHUR DIOXIDE.



#### PRECIPITATION OF TELLURIUM BY SULPHUR DIOXIDE.



one-tenth gram. The sulphur dioxide passed through the solution until thorough saturation. Time of standing about twenty hours. The reaction was conducted in the cold.

#### PRECIPITATION OF SELENIUM AND TELLURIUM BY SULPHUR DIOXIDE.

| Precipitation of   | 0.5    | 1      | 2      | 3      | 5      | 8      | 10     | 20    | Percentage of acidity of solution. |       |
|--------------------|--------|--------|--------|--------|--------|--------|--------|-------|------------------------------------|-------|
| Selenium ... ....  | 0      | .....  | trace  | 0.0124 | ....   | 0.0349 | 0.0935 |       |                                    |       |
| Tellurium... total | 0.0761 | 0.0525 | 0.0653 | 0.0745 | 0.0931 | total  | total  |       |                                    |       |
| Precipitation of   | 30     | 40     | 50     | 60     | 65     | 70     | 75     | 80    | 90                                 | 100   |
| Selenium total     | total  | total  | total  | total  | total  | total  | total  | total | total                              | total |
| Tellurium total    | total  | total  | total  | total  | 0.0965 | 0.0882 | 0.0411 | 0     | 0                                  | 0     |

The accompanying graphical representation of these figures perhaps conveys a more clear idea of the difference of behavior of the two elements.

From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over eighty per cent. acid a separation is possible. We also see that to obtain a total precipitation of the two elements together in this way, the acidity must be confined to definite limits, safely between thirty and fifty per cent.; otherwise one or the other of the two will remain wholly or partially in solution.

If, after saturation with sulphur dioxide, of a selenous acid solution of insufficient acidity, the necessary amount of hydrochloric acid be added, the precipitation becomes total. The same is the case with tellurium in case of insufficient acidity. In case of too high acidity, diluting to the required strength calls forth total precipitation.

The figures for partial precipitation are not absolutely constant. They show variations under different conditions, such as temperature and time of exposure to the action of the reducing agents.

Both elements are more voluminous when precipitated from weak acid solutions than when precipitated from stronger ones.

Ferrous sulphate does not precipitate tellurium.

A series of determinations of selenium, precipitated from solutions of various acidity by ferrous sulphate, showed that the reaction is rapid and quantitative in strong hydrochloric acid. The degree of rapidity of precipitation diminishes as the acidity is reduced. It is total within twenty-four hours as long as the acid is thirty per cent. or more. In fact the reactions of ferrous sulphate and selenous acid are almost identical with those of that acid and sulphur dioxide.

These facts furnish a simple method to separate selenium from tellurium, or any other of the ordinary elements, for analytical or industrial purposes. Gold and silver only, of the metals usually present, interfere. Gold may previously be precipitated by oxalic acid, which does not affect selenium, and silver is so readily separated as chloride that it is no obstacle. Or gold may be precipitated with the selenium and weighed together and the latter dissolved with nitric acid, leaving the gold in

weighable form. Selenium is then obtained by difference.

In attempting to make electrolytic copper determinations in copper residues (from electrolytic tanks), these were treated with strong nitric acid, the silver precipitated as chloride, and filtered. The filtrate, now being freed from gold, silver, and much antimony, was then evaporated to dryness and the residue boiled with hydrochloric acid until the nitrates were fully decomposed. The excess of acid was next neutralized with ammonia, and into the slightly acid solution was conducted hydrogen sulphide. The precipitate, after filtering and washing, was digested with a sodium sulphide solution, and after again filtering and washing, redissolved in nitric acid, made ammoniacal and, for the purpose of precipitating lead and bismuth, ammonium carbonate and phosphate added, and boiled. After cooling and filtering, the ammoniacal copper solution was acidified with sulphuric acid and subjected to electrolysis. It was thought to have been freed of all deleterious elements. The precipitate of copper, however, failed to come down bright and thoroughly adhesive, and on solution with somewhat diluted nitric acid a reddish residue would be visible on the cathode. This proved to be selenium.

The selenium in the same residues was then separated and it was found, by a number of quantitative determinations, that by precipitation with hydrogen sulphide, and subsequent treatment with sodium sulphide, from two-thirds to seven-eighths of the selenium was retained by the insoluble sulphides of copper, bismuth, and lead, the remainder being in the sodium sulphide solution, the latter always containing all of the tellurium.

Looking over many text-books and considerable original literature, I found only one allusion to this fact. William Crookes in his *Select Methods in Chemical Analysis*, p. 426, 1894, says: "Selenium cannot be separated from metals with which it is combined when the sulphides of these metals are insoluble in ammonium sulphide, by making use of the solubility of selenium in this reagent. The insoluble metallic sulphide is almost always mixed with selenide."

Here it should be remembered that the precipitation of selenium, as selenium sulphide,  $\text{SeS}_2$ , from a solution of selenous

acid with hydrogen sulphide, should be conducted in the cold. The precipitate has then a lemon-yellow color and is very readily dissolved by the alkaline sulphide solutions. On heating, this yellow precipitate darkens to an orange color and becomes insoluble. This is said to be due to decomposition and the insolubility of selenium.

Ditte<sup>1</sup> tells us that when selenium and sulphur combine, in the above-mentioned manner, heat is absorbed, or the heat of formation is negative. This sulphide, like hydrogen iodide, belongs, therefore, to a class of compounds which readily decompose.

After a number of qualitative tests, demonstrating that copper, bismuth, and lead, separately retain selenium, to a greater or less extent, according to conditions, the following quantitative determinations were made :

The quantity of selenium in each case was about two grams. This and the varying quantities of copper were in hydrochloric acid solution, with just enough free acid to prevent any precipitation of copper selenite. The precipitation with hydrogen sulphide was conducted under cooling and the resulting precipitate washed with cold water, digested with a strong solution of sodium sulphide, then washed with water containing a few drops of the same reagent, then with water to which a little ammonium sulphide was added, and finally with strong alcohol. Sulphur, selenium, and copper were then determined in the precipitate. The results are given in the table below :

|                | I.<br>Gram. | II.<br>Gram. | III.<br>Gram. | IV.<br>Gram. |
|----------------|-------------|--------------|---------------|--------------|
| Sulphur .....  | 0.3787      | 0.1649       | 0.1730        | 0.0416       |
| Selenium ..... | 0.2828      | 0.1726       | 0.1565        | 0.0239       |
| Copper.....    | 0.980       | 0.4880       | 0.4909        | 0.0979       |

Figuring the theoretical amount of copper, as combined with the sulphur and selenium found, we obtain :

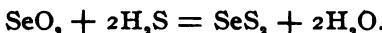
|                         | I.<br>Gram. | II.<br>Gram. | III.<br>Gram. | IV.<br>Gram. |
|-------------------------|-------------|--------------|---------------|--------------|
| Cu combined with S..... | 0.7503      | 0.3267       | 0.3428        | 0.0824       |
| Cu " " Se.....          | 0.2263      | 0.1385       | 0.1256        | 0.0192       |
| Total.....              | 0.9766      | 0.4652       | 0.4684        | 0.1016       |

In another experiment selenium and copper were subjected to the action of hydrogen sulphide in ammoniacal solution, and the precipitate treated as those previously described. The results obtained were :

|                             | Gram.  |
|-----------------------------|--------|
| Sulphur.....                | 0.0098 |
| Selenium.....               | 0.0138 |
| Copper.....                 | 0.0231 |
| Copper (theoretical)        | Gram.  |
| Combined with sulphur ..... | 0.0163 |
| " " selenium.....           | 0.0111 |
| Total.....                  | 0.0274 |

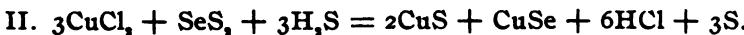
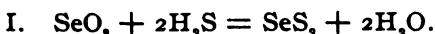
The initial amount of copper in this last case was 0.05 gram, and, as was expected, a large portion remained in the ammonium sulphide solution.

While the results do not appear very satisfactory from the standpoint of analytical accuracy, it should be stated that the purpose of the determinations was to find the existence or non-existence of a definite reaction, and the molecular proportions of the sulphide and selenide formed. At first sight the results might be considered of a negative character. On closer observation, however, two out of the first four determinations show a maximum of selenide, or a minimum of sulphide formation, in which the atomic ratio of selenium and sulphur is approximately 1 : 2, or the same as in selenium sulphide, as formed by the reaction of selenous acid and hydrogen sulphide.



By the precipitation in ammoniacal solution the contents of selenium in the precipitate are higher. It is quite likely, however, that in this case more of the copper sulphide than of the selenide was held in solution by the ammonium sulphide, and it is clear that in acid, as well as in alkaline, solution only a certain maximum quantity of copper selenide is formed which never equals the amount (molecularly) of copper sulphide.

According to the above it may plausibly be supposed that the reaction takes place in two stages :



For this theory there is no positive proof; but it is plain that the hydrogen sulphide must reduce both copper chloride and selenous acid, that copper and selenium may combine in their nascent state, and that sulphur is precipitated, or that copper may combine with previously formed selenium sulphide, and that this also must be accompanied by sulphur precipitation.

The reaction appears one of the most interesting in inorganic chemistry and deserves further investigation.

BALTIMORE COPPER WORKS, July, 1897.

## COMPOSITION AND FORMATION OF TANK RESIDUES IN ELECTROLYTIC COPPER REFINERIES.

BY EDWARD KELLER.

Received July 30, 1897.

THE production of electrolytic copper and its separation of other metals by means of the electric current, was first established on a commercial scale by James B. Elkington, of England. In two patents, No. 2,838, Nov. 3, 1865, and No. 3,120, Oct. 27, 1869, he laid down all the essential points of the processes which guide the operations at the present day.

The original object of the process was mainly the separation of the precious metals from the copper. The production of a pure copper from the crude metal is, however, now equally important. The process may be described briefly as follows: The crude copper is cast into anodes of generally six to eight square feet by one to one and one-half inches in thickness. These are suspended in tanks, alternating with thin sheets of pure copper, as cathodes, one to two inches apart. Of the cathodes there is one more in number than of the anodes. In the tanks the electrolyte, in which anodes and cathodes are submerged, is forced to circulate in order to maintain uniform density. This electrolyte is said to be generally a solution of three per cent. copper (as sulphate) with six per cent. of free sulphuric acid.

Each anode is connected with the conductor from the positive pole of the dynamo, each cathode with the negative. If the number of anodes in one tank be  $n$ , we have  $n$  branches of the electric current from the positive pole, and  $n+1$  from the negative. Anodes and cathodes being otherwise insulated, the current must pass from anode through the electrolyte to cathode,

dissolving the copper of the former and depositing it on the latter. The same current passes through a series of tanks, which may number many hundred.

The system described is called the "multiple." The "series" system is a later invention. It differs from the former, that in each tank there is at one end but one anode connected with the positive pole, and at the opposite end but one cathode with the negative. The space between is filled with rolled copper plates, set vertically, all a certain distance from each other. Electrolyte and circulation are the same as in the other system. When the electric current passes through this system, each surface of the individual plates facing the anode becomes a cathode surface, and that facing the cathode becomes an anode surface, so that the copper dissolved on the anode surface of each plate is deposited on the opposite, or cathode surface of the next plate.

Details of the series system, with illustrations, may be seen in the papers of United States patents No. 377,487, Feb. 7, 1888, and No. 459,838, Sept. 22, 1891, secured by Mr. Edward S. Hayden, of Waterbury, Conn.

The precious metals and part of the impurities of the dissolved anodes, in either system, fall to the bottom of the tanks, forming there a sediment or residue, frequently also called slimes, mud, etc.

It is the object of this paper to show how some of these latter products are composed and to what extent the various impurities in the anode copper take part in their formation.

In the following are given partial analyses (oxygen and hydrate water were not determined) of residues from copper derived from ores from Butte, Mont., as also the composition of the corresponding anode copper. The copper of I was made by the reverberatory, of II by the converter process:

|           | I.                              |                        |
|-----------|---------------------------------|------------------------|
| Residues. |                                 | Anode copper.          |
| Ag....    | 53.894 per cent. = 15718.7 ozs. | 100.1 ozs.             |
| Au....    | 0.2959 " " = 86.3 "             |                        |
| Cu....    | 11.010 " "                      |                        |
| Pb....    | 0.910 " "                       | 0.0093 per cent.       |
| Bi....    | 3.930 " "                       | 0.0320 " "             |
| Sb....    | 6.250 " "                       | 0.0651 " "             |
| As....    | 2.107 " "                       | 0.0586 " "             |
| Se....    | 0.394 " "                       | Se and Te.. 0.0098 " " |

|                                  | Residues.       |   | Anode copper. |
|----------------------------------|-----------------|---|---------------|
| Te ....                          | 1.174 per cent. |   |               |
| SO <sub>4</sub> ...              | 5.268 "         | " |               |
| H <sub>2</sub> O <sup>1</sup> .. | 2.365 "         | " |               |

## II.

|                       | Residues.                        |          | Anode copper.    |
|-----------------------|----------------------------------|----------|------------------|
| Ag....                | 55.150 per cent. = 16085.04 ozs. |          | 100.47 ozs.      |
| Au....                | 0.198 " " =                      | 57 749 " |                  |
| Cu....                | 13.820 "                         | "        |                  |
| Pb....                | 2.070 "                          | "        |                  |
| Bi....                | 0.340 "                          | "        | 0.0035 per cent. |
| Sb....                | 2.440 "                          | "        | 0.0510 " "       |
| As....                | 1.090 "                          | "        | 0.0180 " "       |
| Se....                | 0.718 "                          | "        |                  |
| Te....                | 0.892 "                          | "        |                  |
| Fe....                | 0.800 "                          | "        |                  |
| SO <sub>4</sub> ...   | 10.680 "                         | "        |                  |
| H <sub>2</sub> O... . | 2.604 "                          | "        |                  |

The figures in I represent the average of nearly a one year's run; in II a three months' run in the same refinery.

In the formation of these residues the anodes contribute all their contents in silver, gold, selenium, and tellurium. From any one of these elements we are, therefore, enabled to compute their degree of concentration in the residues, and to figure the amount of partial deposition therein of the other elements.

Since silver constitutes by far the greatest quantity, and consequently its determination being the most accurate, it is best to proceed from it. We then have:

|          | I.        |               |                |
|----------|-----------|---------------|----------------|
|          | Residues. | Anode copper. | Concentration. |
|          | Ounces.   | Ounces.       |                |
| Ag ..... | 15718.7   | 100.1         | 157            |
|          | II.       |               |                |
|          | Residues. | Anode copper. | Concentration. |
|          | Ounces.   | Ounces.       |                |
| Ag ..... | 16085.05  | 100.47        | 160            |

Dividing the percentages in residues of partially deposited elements by the figures for concentration, we obtain the percentages of the original quantity in the anodes deposited in the residues. The difference between this and the total contents in the anodes is the amount gone into solution in the electrolyte.

<sup>1</sup> The sample was dried at the temperature of boiling water, and the remaining water determined at 250° C.

From the latter, practically all the copper dissolved from the anode is deposited on the cathode, carrying with it but a few per cent. of the impurities in solution.

Proceeding according to the above, we obtain the following :

## I.

| Contents of anodes. | Per cent. | Amount of original contents in anodes<br>gone into residue and solution. |              |
|---------------------|-----------|--|--------------|
|                     |           | In residue.  | In solution. |
| Cu.....             | 99.3      | 0.07   | 99.93        |
| Bi .....            | 0.0320    | 78.22  | 21.78        |
| Sb .....            | 0.0651    | 61.14  | 38.86        |
| As .....            | 0.0586    | 22.90  | 77.10        |

## II.

|          | Per cent. | Per cent. | Per cent. |
|----------|-----------|-----------|-----------|
| Cu.....  | 99.4      | 0.086     | 99.914    |
| Bi ..... | 0.0035    | 60.71     | 39.29     |
| Sb ..... | 0.0510    | 29.90     | 70.10     |
| As ..... | 0.0180    | 37.84     | 62.16     |

Lead is not considered in these figures, because lead-lined tanks and lead sulphate, carried by the commercial sulphuric acid employed, render the obtaining of correct results impossible.

There is little similarity between the compositions of I and II. In I the quantities of bismuth, antimony, and arsenic in the anodes are not very widely different. Bismuth shows the least solubility, arsenic the greatest. In II, where antimony greatly preponderates in the anodes, that element also shows the greatest solubility.

The ratio of selenium and tellurium in the two samples of residues may be worthy of notice. We have for I, 1 : 3; for II, 7 : 9. The current opinion, that selenium is merely a minor companion-element to tellurium in our western copper, seems thereby proven to be erroneous.

The ratio of the two elements in the anode copper is without doubt the same, and as they have never been separated from copper for quantitative determination individually, it can readily be shown by dividing their percentages in the residues by the figure of concentration what their quantities are in the corresponding anodes. We find :

## IN ANODES.

|            | I.<br>Per cent. | II.<br>Per cent. |
|------------|-----------------|------------------|
| Se.....    | 0.00251         | 0.00449          |
| Te.....    | 0.00748         | 0.00558          |
| Total..... | 0.00999         | 0.01007          |

The total of the two elements thus calculated, 0.0999 per cent., for I, corresponds closely with the actual amount, 0.098 per cent., found in the anodes. For II no direct determination was made in the anodes.

BALTIMORE COPPER WORKS, July, 1897.

## SOME PRODUCTS OF THE TUBERCULOSIS BACILLUS.

BY E. A. DE SCHWEINITZ AND MARION DORSET.

Received June 17, 1897.

TUBERCULIN, as is well known, is the extract of the tuberculosis bacilli, including the media upon which they are grown. From specially prepared artificial cultures of the tuberculosis germ, Kühne and independently one of us,<sup>1</sup> obtained a substance corresponding to a nucleo-albumin, which appears to be the fever-producing principle of the germ. However, many conditions in tuberculosis were not accounted for by this substance, and as Mafucci, Prudden and Hodenpeyl, Vissman, and others, had succeeded in producing tubercular nodules without necrosis by the intravenous injection of dead bacilli, it seemed as though it should be possible to isolate either from cultures or from bodies of the germs themselves, some substance which might be considered accountable for the coagulation necrosis of tissue which takes place, a necrosis which appears necessary for the progress of the disease. This problem was undertaken by my assistant, Dr. Dorset, and myself more than two years ago. After many fruitless attempts we succeeded in isolating from artificial cultures a crystalline substance, having a melting-point of 161°–164° C., readily soluble in ether, alcohol, and water, which separated from these solutions in needle-like or prismatic crystals, showing a slight yellow tint. They did not give the biuret reaction. The solution of this substance has an acid reaction to litmus, is acid in taste, and is optically inactive. The crystals give no precipitate with silver nitrate, platinic chloride, or barium hydroxide. The analy-

<sup>1</sup> DE SCHWEINITZ; Bulletin No. 7, Bureau of Animal Industry.

sis showed carbon 50.88 per cent., hydrogen 6.70 per cent., oxygen 43.42 per cent., giving a formula corresponding closely to C<sub>18</sub>H<sub>30</sub>O<sub>4</sub>. This is the formula of teraconic acid, an unsaturated acid of the fatty series.

The culture media upon which the germs were grown and from which these crystals were obtained, contained potassium acid phosphate, ammonium phosphate, asparagin, or the solution of these salts without asparagin, and glycerol, the medium used by one of us (de Schweinitz)<sup>1</sup> some years ago for studying these germs. After the germs have been growing on this medium for some weeks the liquid becomes light yellow in color, having the appearance of a pale urine, a change which does not take place in the uninoculated medium kept under the same conditions. Efforts to obtain this same acid from the ordinary beef broth cultures containing peptone and glycerol resulted in securing minute amounts of the crystals only, which it was never possible to purify. After noting some of the other properties of this acid substance we came to the conclusion that the presence of peptone and the nitrogenous bases of the meat resulted in their combination with the crystals forming compounds from which the acid could not again be easily extracted, even after the addition of acid. Finally, a small quantity of the crystalline substance obtained from the artificial cultures was added to the glycerol peptonized beef broth medium, but it was impossible to recover it again by the methods used for the first extraction, viz., repeated precipitation with alcohol, solution in water and extraction with ether. The ready solubility of this substance in water, as well as ether, probably accounts for the difficulty of obtaining it. The uninoculated medium did not yield these crystals. When dissolved in water and injected into guinea pigs, this substance caused a reduction of temperature and necrosis of the areas with which it came in contact. As this had been observed in a number of experiments, the idea was suggested that this acid, evidently a secretion of the germ, was one of its most powerful weapons, that by its action upon the tissue the cells were first destroyed so that they could subsequently be utilized by the germ as food, and in this way the germ protected itself from surrounding leucocytes. To test this, crystals dis-

<sup>1</sup> *New York Medical Journal*, 1893.

solved in sterile water were injected by means of a hypodermic syringe directly into the liver tissue of a guinea pig. At the same time the same quantity of water was injected into a check in the same way. After forty-eight hours, check and experimental animals were killed. The check failed to show any effect, while the others exhibited a liver with several light spots and necrotic areas. Repetition of this experiment gave the same results.

No effort was made to recover these crystals from the liver as the amount used was too small. As the growth of the tuberculosis bacillus in the body is localized and where localized the necrotic areas are apparent, the fairest test was to bring the substance as soon as possible in contact with the liver tissue.

It seems very reasonable to conclude that we have here the substance formed by the tuberculosis germ, which is responsible for the coagulation necrosis in this disease. The formula which can be deduced from the analysis makes this acid correspond closely to teraconic, which has properties very similar to those noted by us in connection with this new acid. Its identity we have not yet proved or disproved. The amount of this acid obtainable is very small, so that we have used only a very small portion of it for testing its immunizing property. A single injection of 0.0020 gram was sufficient to keep the animals alive some weeks longer than the checks, and its solution appeared to exert some slight bactericidal influence.

As this substance seemed to be a temperature-reducing principle in healthy and diseased animals, we endeavored to separate from tuberculosis cultures the fever-producing principle. The crystals were always found in the culture liquid and only minute amounts could be obtained from the germs themselves that had been grown on liquid media. Accordingly, these germs carefully filtered without heat, were washed with cold water and next extracted with hot water. This hot water extract contained an albuminoid which caused the tuberculin reaction in tuberculous guinea pigs and calves upon repeated injections.

Roux and Nocard claim that they have a tuberculin which will give reactions almost indefinitely, but do not describe its method of preparation. Whether this is the same substance that we have obtained we are unable to say, but certain it is that the tuberculin prepared in the way we have indicated will

give reactions four or five times in succession where the reaction with tuberculin, as prepared in the ordinary way, fails after the second time. The conclusion is a fair one, we think, that the fever-reducing principle having been removed to an extent, if not entirely, the immunity to the fever-producing principle is much more slowly acquired. In the *Deut. Med. Woch.*, April 1, 1897, Dr. R. Koch describes some new tuberculin preparations. The dried tuberculosis bacilli were taken (the culture medium used is not mentioned), finely powdered, and centrifugalized with distilled water. The opalescent solution obtained tested upon animals gave the tuberculin reaction. The residual germs were submitted to this treatment a number of times until finally all were practically dissolved. The latter solutions, he said, in large doses caused a reaction, but in small quantities did not produce this result, and seemed to exert both an immunizing and curative action in experimental tuberculosis. Koch used for this work virulent germs and claims that attenuated germs do not give an active product. Our work was done with germs purposely attenuated by cultivation and the results show that a very active fever-producing, fever-reducing, and probably curative principle can be obtained from them. It hardly seemed justifiable to ourselves to powder dried virulent germs and have the dust floating in the air. Koch further refers to two fatty acids, which, in conjunction with Proskauer, had been found in the bodies of the germs. The writers of this paper published in this Journal, August, 1895, a preliminary study of the fats of the tuberculosis bacilli, showing the high content of the fat in the body of these germs, which accounts for the difficulty in staining them with certain colors, as well as their difficult absorption. In a later paper<sup>1</sup> we described briefly the different acids obtained from these fats, both high-melting and low-melting. Whether these are identical with the acids referred to by Koch we are unable to say, from the brief description he has so far given. This interesting necrotic acid, which plays so important a part apparently in the progress of tuberculosis, and the fever-producing principle formed by the tuberculosis germ are receiving further chemical study. Their physiological importance is very great. The acid may be tentatively called tuberculinic acid.

BIOCHEMIC LABORATORY, WASHINGTON, D. C.

<sup>1</sup> *Centrbl. Bak. u. Parasit.*, 19, 18, 19, 707.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN.]

FURTHER STUDY ON THE INFLUENCE OF HEAT TREAT-  
MENT AND CARBON UPON THE SOLUBILITY OF  
PHOSPHORUS IN STEEL.

BY E. D. CAMPBELL AND S. C. BABCOCK.

Received June 29, 1897.

A BOUT a year ago we published a paper upon the same subject as that of the present research.<sup>1</sup> At the time of our previous work we did not have a pyrometer on which we could depend, so that we were unable to state with accuracy the exact treatment to which the material under examination had been subjected. Since the time of our previous work we have obtained an accurate Le Chatelier pyrometer so that we have been able to heat specimens up to 1,100°, with probable error of not over 5°.

The heat treatment to which the specimens in the table given below were subjected are as follows: The metal called "annealed" was raised to between 900° and 1,000° and then allowed to cool slowly. The specimens called "quenched from  $x^{\circ}$ " were placed in a porcelain-lined iron tube with the thermal junction of the Le Chatelier pyrometer in contact with the specimen. The portion of the tube containing the specimen was slowly heated by means of a Hoskins' Gasolene Furnace until the desired temperature was reached. The time required for heating the specimens was usually from twenty-five to forty minutes. When the desired temperature was reached, the tube was tilted up so that the specimen dropped directly into ice-water at a temperature of from 4° to 5°. The specimens so prepared were then either drilled or pounded sufficiently fine to enable them to be used for chemical examination.

The method of analysis employed is somewhat different from that described in our previous paper. Instead of treating first with neutral mercuric chloride, then after filtering and washing the precipitated mercury, treating this latter with four per cent. hydrochloric acid, and finally volatilizing the mercury and determining the phosphorus in the residue, we have shortened the

<sup>1</sup> *Am. Chem. J.*, 18, 719.

process and determined only the phosphorus soluble in a slightly acid solution of mercuric chloride. The objections to the process employed last year are principally, the length of time necessary for handling the precipitates, and to a less extent the fact that the amount of phosphorus soluble in hydrochloric acid increases somewhat with the time of digestion, thus necessitating the adoption of an empirical length of time of treatment with the reagent. In the method which we have employed in the present work, we have demonstrated by numerous experiments that the length of time of standing has no appreciable effect on the solubility of the phosphorus in a given sample. A specimen digested one and one-half hours gave 0.096 per cent. soluble, while another sample of the same specimen gave 0.093 per cent. after standing forty hours.

The special solutions employed in the determination of the soluble phosphorus were as follows: The 'two per cent. hydrochloric' is twenty cc. hydrochloric acid (sp. gr. 1.20) made up to one liter. The ferric chloride solution is 8.15 grams of iron wire containing 0.050 per cent. phosphorus dissolved in 1.20 nitric acid, boiled, and evaporated to dryness with excess of hydrochloric acid, sufficient to convert it to ferric chloride. After evaporation to dryness the ferric chloride was taken up with twenty-five cc. hydrochloric acid, transferred to a 250 cc. flask, and made up to the mark. Five cc. of this solution contains five-tenths cc. of free hydrochloric acid and sufficient phosphorus to give five milligrams precipitate of ammonium phosphomolybdate, which amount was deducted from the weight of the precipitates obtained in the course of the work. The ammonium acetate solution was made by dissolving 400 grams of ammonium acetate in 800 cc. of water.

The method employed is as follows: Five grams of the steel is introduced into an Erlenmeyer flask and thirty-five grams of powdered mercuric chloride added; to this is further added 100 cc. of two per cent. hydrochloric acid and the flask tightly stoppered. The whole is allowed to stand, with occasional shaking, for one and one-half hours, or until solution is complete. The solution is then filtered by aid of a pump and the precipitated mercury washed four times with hot water. A convenient method for filtering and washing the precipitated mercury is to

employ a perforated porcelain disk about four cm. in diameter, held in a funnel. On this is placed one filter paper just the size of the disk, and a second one on top being slightly larger. After fitting the upper one by wetting and pressing down firmly a small amount of finely divided asbestos, suspended in water, may be poured on, which will serve to make the points tight and facilitate the removal of the paper and mercury after washing.

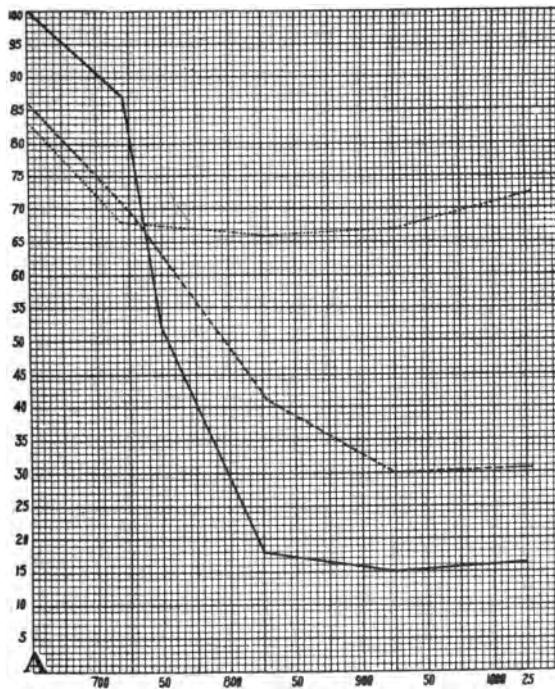
To the filtrate and washings from the precipitated mercury, amounting to 200 to 225 cc., is added five cc. of the ferric chloride solution and fifteen cc. of the ammonium acetate. The whole is then covered in lipless beakers and brought almost to a boil, when the basic acetate carrying ferric phosphate is precipitated. The solution is then filtered and allowed to drain without washing. The filter containing the basic acetate is transferred to the beaker in which the precipitation was made and heated with twenty cc. of strong nitric acid until the solution is complete. After diluting with twice its volume of water, the filter paper is filtered out and washed with hot water, acidified with nitric acid, and the solution boiled down and the phosphorus precipitated with ammonium molybdate. From the weight of the ammonium phosphomolybdate weighed on asbestos funnels, dried at 120°, is deducted five milligrams for the phosphorus contained in the ferric chloride solution used, and the per cent. of the phosphorus soluble is then calculated.

The results obtained on three specimens of steel are given in the following table :

| Name<br>of<br>steel. | Chemical composition. |       |       |      |      | Heat treatment. | Quenching<br>temperature. | Percent of<br>phosphorus<br>soluble in<br>acid HgCl <sub>2</sub> | Percent of<br>total phos-<br>phorus sol-<br>uble in acid<br>HgCl <sub>2</sub> |
|----------------------|-----------------------|-------|-------|------|------|-----------------|---------------------------|--|---|
|                      | C.                    | P.    | Mn.   | S.   | Si.  |                 |                           |  |   |
| C1 5                 | 0.10                  | 0.119 | 0.484 | .... | .... | annealed        | ....                      | 0.099  | 83.2  |
| C1 5                 | 0.10                  | 0.119 | 0.484 | .... | .... |                 | 719°                      | 0.081  | 68.08   |
| C1 5                 | 0.10                  | 0.119 | 0.484 | .... | .... |                 | 825°                      | 0.079  | 66.4  |
| C1 5                 | 0.10                  | 0.119 | 0.484 | .... | .... |                 | 928°                      | 0.080  | 67.2  |
| C1 5                 | 0.10                  | 0.119 | 0.484 | .... | .... |                 | 1028°                     | 0.086  | 72.2  |
| N.S. 5               | 0.37                  | 0.160 | 0.820 | .... | .... | annealed        | ....                      | 0.137  | 85.6  |
| N.S. 5               | 0.37                  | 0.160 | 0.820 | .... | .... |                 | 728°                      | 0.110  | 68.8  |
| N.S. 5               | 0.37                  | 0.160 | 0.820 | .... | .... |                 | 827°                      | 0.066  | 41.2  |
| N.S. 5               | 0.37                  | 0.160 | 0.820 | .... | .... |                 | 923°                      | 0.048  | 30.0  |
| N.S. 5               | 0.37                  | 0.160 | 0.820 | .... | .... |                 | 1027°                     | 0.049  | 30.6  |

| Name of steel. | C.   | P.    | Mn.   | S.    | Si.   | Chemical composition. | Heat treatment. | Quenching temperature. | Percent. of phosphorus soluble in acid HgCl <sub>2</sub> . | Per cent. of total phosphorus soluble in acid HgCl <sub>2</sub> . |
|----------------|------|-------|-------|-------|-------|-----------------------|-----------------|------------------------|--|---|
| Car. I         | 1.22 | 0.098 | 0.780 | 0.068 | 0.058 | annealed              | ....            | 0.098                  | 100.0  |   |
| Car. I         | 1.22 | 0.098 | 0.780 | 0.068 | 0.058 |                       | 719°            | 0.087                  | 89.8   |   |
| Car. I         | 1.22 | 0.098 | 0.780 | 0.068 | 0.058 |                       | 750°            | 0.051                  | 52.0   |   |
| Car. I         | 1.22 | 0.098 | 0.780 | 0.068 | 0.058 |                       | 825°            | 0.018                  | 18.3   |   |
| Car. I         | 1.22 | 0.098 | 0.789 | 0.068 | 0.058 |                       | 923°            | 0.015                  | 15.3   |   |
| Car. I         | 1.22 | 0.098 | 0.780 | 0.068 | 0.058 |                       | 1023°           | 0.016                  | 16.2   |   |

The evident influence of the amount of carbon present and the heat treatment upon the solubility of the phosphorus as given in the last column of the above table is best shown graphically in the diagram given below.



Full line = Carnegie Iron.

Broken line = N. S.

Dotted line = Cleveland.

The above work brings out the fact that phosphorus like carbon is capable of existing in steel in at least two forms and that

the influence of phosphorus upon the physical properties of steel in which it is contained is as much dependent upon the form of combination in which it exists as upon the quantity. This power of phosphorus to exist in two or more forms in steel with the varying influence on the brittleness of the steel according to the form present will, we think, account for many of the apparent inconsistencies in the statements usually made by metallurgists in regard to the behavior of this element. Much remains to be done upon the products of solution of iron and steel along the lines indicated either by the present paper or by that of Mackintosh,<sup>1</sup> or more recently by Juptner's paper, read before the British Iron and Steel Institute, May, 1897, before we shall be able to accumulate sufficient data to enable us to draw reliable conclusions as to the forms in which phosphorus may exist in iron and steel, the conditions under which the different forms are produced, and the influence of the different forms on the physical properties of the metals.

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#### AN ELECTRICAL LABORATORY STOVE.

By M. D. SOHON.

Received July 7, 1897.

**T**HIS apparatus has been designed to economically replace, as far as possible, the ordinary water-baths and gas burners used in the laboratory.

The stove is of copper, preferably cylindrical, about three

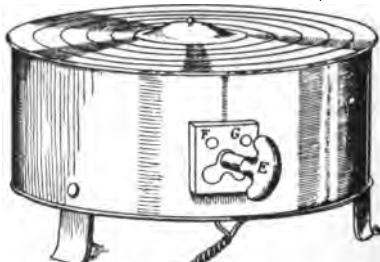


FIG. I.

inches in height, exclusive of legs, and seven and a half inches in diameter. The top consists of the usual concentric rings; the bottom is open. The heating plate *A* is placed two inches

<sup>1</sup> *Trans. Amer. Inst. Min. Eng.*, 14, 385.

from the top, allowing ordinary flasks and casseroles to rest securely on the rings without touching the bottom. There is a clearance of one-fourth inch between the plate and sides of stove, allowing anything falling into the stove to pass through. The heating plate and body are independently fastened to the legs and may be quickly detached.

The heat is generated by the coils, *B*, of ordinary rheostat alloy, imbedded in silicate insulation, a half inch asbestos board, *C*, supports this and prevents the radiation of heat downward. A copper plate, *D*, turned over the edges, protects the coils and insulation from materials falling upon them, and strengthens the plate. Copper is preferable to the iron plate usually employed in rheostats, heating more rapidly and being less quickly attacked by reagents, and is easily replaced if destroyed.

The heating coil is in two parts of unequal size, either or both

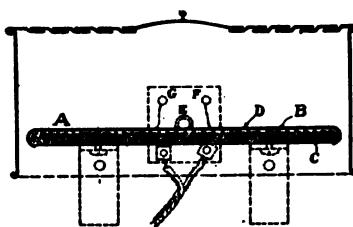


FIG. 2.

of which may be brought into use by means of the switch *E*, thus permitting of three variations of temperature without the use of other apparatus. The most convenient size of coils are such as to maintain the plate at about 90°C., 110°C., and 125°C.

Compared with the water-bath it is clean and dry and requires no attention. It is only necessary to *press the button* and it supplies immediately a constant and dry heat. The heat can be varied, and it is not affected by draught as are gas stoves, nor does it unnecessarily heat the laboratory. By the use of suitable coils or interposing resistance, the stove may be used with more volatile liquids. It especially recommends itself in connection with the distillation of inflammable liquids, extractions, etc., where danger from fire is to be avoided.

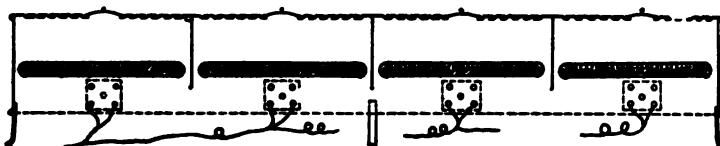


FIG. 3.

A group of the stoves, independently connected, is highly preferable to the large cumbersome water- or steam-baths generally employed.

### THE ESTIMATION OF PHOSPHORUS IN STEEL.

BY R. W. MAHON.

Received August 12, 1897.

MANY analysts regard the titration of ammonium phosphomolybdate by standard alkali and acid with phenol phthalain as indicator as the best method for the routine determination of phosphorus in steel.

By two modifications of one of the approved processes for obtaining phosphorus in steel as ammonium phosphomolybdate, I have so shortened the operations as to enable one to execute the analysis in eight minutes, from receiving the drillings to obtaining the result. The results are accurate in the absence of arsenic. I have not experimented with the process in the presence of arsenic. No experiments have been made with steels containing silicon or carbon in considerable quantity. The process was devised for facile determination of phosphorus in steel containing scarcely any silicon, and low in carbon. It appears entirely probable that with high carbon and silicon, perfectly accurate results would be obtained. The two modifications I have to suggest are (1) effecting the partial neutralization in a different manner, and (2) precipitating at a higher temperature. Before the steel drillings are received, the following preparations for the analysis are made: Seventy cc. of water and thirty cc. of nitric acid (sp. gr. 1.4) are poured into a sixteen-ounce Erlenmeyer flask, a measured quantity of standard caustic potash solution and a little water are poured into a small beaker, the reading of the acid burette is recorded, and the filter is placed in its funnel, at the suction-pump, ready for use.

Four grams of drillings are placed in the flask containing the

acid, and this immediately placed over the gas. As soon as dissolved add three cc. of a standard solution of potassium permanganate, and boil until no longer pink. Add ten cc. of hydrochloric acid (sp. gr. 1.20), boil until clear, remove from gas, wait for a few seconds until the boiling has nearly ceased, and then add a mixture of fifty cc. of molybdate solution and ten cc. to fifteen cc. of ammonia (sp. gr. 0.90), made ready just before use. Pour into the middle of the flask, not down the side. Twirl the flask in both directions, successively, without delay. Shake the open flask for about one quarter of a minute. Filter and wash with cold water. Place the paper and precipitate in the beaker, containing an excess of caustic potash solution, add phenol phthalein, and determine the excess of caustic by the standard acid.

The two standard solutions are of the customary strength; the molybdate solution is made according to the following formula: 100 grams of molybdic acid are dissolved in a mixture of 200 cc. of ammonia (sp. gr. 0.90) and 200 cc. of water, and the solution filtered into 1,250 cc. of nitric acid (sp. gr. 1.20), blowing air through the mixture. Fifteen cc. of ammonia (sp. gr. 0.90) will neutralize fifty cc. of this solution, hence the amount of ammonia recommended in making up the mixture for use in an analysis. Ten to fifteen cc. of ammonia can be added, and if the mixture is kept cool during mixing no separation of molybdic acid will occur for some undetermined, but considerable time. This cold mixture can be satisfactorily used. It is, however, unnecessary to take the precaution of cooling during the mixing of molybdate solution and ammonia, if the mixture is used as directed. It is to be noted here that the graduated or other vessel used for mixing should invariably be rinsed before being used for a second quantity, as neglect of this sometimes causes separation of molybdic acid. The object of adding the mixture by pouring it into the middle of the solution and at once shaking the flask is to prevent separation of molybdic acid. This is the more elegant way of working, but is not indispensable, as the molybdic acid precipitated by very solid addition of the mixture, not poured accurately into the center, at once goes into solution again, when the prescribed course of manipulation is followed.

The temperature of the solution at the moment of addition of molybdate is about 105°C. The temperature of the mixture added is about 60°C. The amount of free acid before the molybdate is added is such that eighteen to twenty cc. of ammonia (sp. gr. 0.90) would, if added, produce a decided precipitate: A standard steel in which phosphorus had been determined many times with elaborate care by the molybdate-magnesia method, as 0.108, was used to make two series of estimations, titrating ammonia phosphomolybdate by standard caustic solution, one (A) with the older method of precipitating—that is adding ammonia in excess to the cooled solution of the steel, acidifying with nitric acid, and bring to 75° C. before adding molybdate solution; the other (B) with the method of precipitating described above—that is mixing molybdate solution and ammonia, in definite quantities, and precipitating a few seconds after removal from lamp.

Four estimations varying from 0.107 to 0.110.

(A).

0.108  
0.107  
0.110  
0.107

Mean, 0.108

Twelve estimations varying from 0.108 to 0.111.

(B).

0.108  
0.111  
0.109  
0.111  
0.109  
0.109  
0.109  
0.110  
0.109  
0.110  
0.109  
0.111

Mean, 0.110

In the series (B) above, the determinations were made to study the value of this method of precipitation, not to prove the time needed, a number of the estimations having been made simultaneously; consequently the filtration was only made immediately in some of the number.

In the following the time needed was the principal object of study, and each filtration was made a few seconds after adding molybdate:

| Time consumed in analysis.    | Phosphorus.<br>Per cent. |
|-------------------------------|--------------------------|
| Eleven minutes .....          | 0.108                    |
| Ten minutes .....             | 0.107                    |
| Eight and a half minutes..... | 0.107                    |

I have also carried out one, adding the potassium permanganate before the last few particles of steel had dissolved, and only boiling until the pink color nearly disappeared.

| Time consumed in analysis. | Phosphorus.<br>Per cent. |
|----------------------------|--------------------------|
| Seven minutes .....        | 0.109                    |

Although successful here, this last procedure might fail with high carbon steel. All of the foregoing filtrates remained perfectly clear. The quantity of ammonia recommended is a vital point.

#### ESTIMATIONS BY METHOD B VARYING THE QUANTITY OF AMMONIA.

|                            | Phosphorus.<br>Per cent. |
|----------------------------|--------------------------|
| Five cc. of ammonia .....  | 0.096                    |
| Twenty cc. of ammonia..... | 0.113                    |

#### ESTIMATION BY METHOD B WITH VARIATION IN THE TEMPERATURE OF PRECIPITATION.

|  |  |
|--|--|
| 75° C., 0.110 per cent. phosphorus filtered in one minute. |  |
| 65° C., 0.103 " " " " hour.                                |  |
| 35° C., 0.108 " " " " twenty-four hours.                   |  |

This method of working is now in daily use, having been repeatedly checked by the older style, invariably with entire satisfaction. Used as a rapid method and with the details of manipulation described, the results are identical with those by (A). My principal use of it has been simply to lessen the number of operations needed; used in this way the drillings are placed in an empty flask, and the acid and water poured upon them; the filtration not necessarily being made after a fraction of one minute, nor with the suction-pump at all, but with the use of funnel and platinum cone, and filtering after the lapse of an indefinite time, varying from a few minutes to hours. Used thus, the results are 0.002 per cent. phosphorus higher.

The caustic solution is empirically standardized in these experiments by precipitates made in the older way (A); hence these appear as correct, and those by (B) as 0.002 per cent. phosphorus high. Were (B) precipitates used in standardization the record would make the results by (B) appear as correct, while those by (A) would average 0.106.

## THE DETECTION OF FOREIGN FATS IN LARD AND BUTTER.

BY C. B. COCHRAN.

Received August 12, 1897.

A S a means of detecting beef fat in lard I have made use of the following process.: In a glass-stoppered twenty-five cc. graduated cylinder are introduced two cc. of the melted fat, and to this is added twenty-two cc. of fusel oil. The contents of the cylinder are warmed to about blood heat in order to obtain a perfect solution, and then allowed to cool slowly to a temperature of 16° to 17°C. This final temperature is maintained for two or three hours, during which time a crystalline deposit takes place, the amount and character of which varies with the fat under examination.

The deposit is then transferred to a filter paper and the fusel oil allowed to drain off as completely as possible. A part or the whole of the residue on the filter paper is then transferred to a test-tube and dissolved in ether. The mouth of the tube is closed with a plug of cotton and the crystals which form on standing are mounted in a drop of cottonseed oil and subjected to microscopic examination. By this method I have been able to detect the presence of a smaller amount of beef fat than I could detect when the sample was directly crystallized from ether.

A sample of lard containing ten per cent. of beef fat, when treated in this manner, will furnish a microscopic field showing abundant typical crystallizations of beef fat, which are usually much more numerous than lard crystals. When twenty per cent. of beef fat are present I have been unable to detect any lard crystals.

When the lard under examination contained five per cent. of oleostearin the crystals, although somewhat modified both in shape and manner of aggregating, yet gave decided evidence of the presence of beef fat.

A sample of lard containing two per cent. of oleostearin gave crystals so nearly like those formed from pure lard that I felt unable to say that the appearance either of the clusters or of the individual crystals indicated the adulteration.

Mutton tallow forms crystals very similar to those from beef.

So far as I know the one cannot be distinguished from the other by the character of the crystallization. All that has been said of beef fat in lard would apply also to mutton fat. The latter named fat behaves in lard like the former.

The amount of the deposit obtained from the fusel oil solution at 17°C. varies according to the character of the fat. A sample of beef suet, treated as indicated, gave a deposit of sixteen cc. The deposit obtained from a sample of oleostearin filled the tube to the level of the liquid. Pure lard in no case gave a deposit of over four cc. The relation between the amount of the deposit and the character of the fat is shown in the accompanying table and suggests a possible means of approximately estimating the percentage of beef tallow in lard, especially when taken in connection with the melting-point of the sample. Two or more pure lards of known melting-point, one high, the other low, could be kept as standards for comparison. The amount of deposit and melting-point of the sample of unknown origin compared with the deposit and melting-point of the standard would furnish a basis of comparison, as is done in the process devised by W. R. Stock. Before reading the amount of the deposit it is well to shake the cylinder, after which the deposit will settle evenly and more compactly.

The melting-points found in pure pig fats, given in the table, vary from 34°C. to 45°C., which is a little wider range than that given in the publications on lard by the United States Agricultural Department. The samples taken from different parts of the animal were all rendered in the laboratory and the melting-points determined by my assistant, Mr. C. S. Brinton. The method adopted by the Association of Official Agricultural Chemists was followed in detail in all cases.

In examining samples of butter or oleomargarine, add eight cc. of fusel oil to two cc. of the filtered fat; warm until a perfect solution is obtained, then cool to 16° or 17°C. A deposit will be formed which, in the few experiments I have made, has been greater in the case of oleomargarine than in butter. When this deposit is crystallized from ether very perfect crystals of large size are obtained. Up to the present time I have only examined six samples by this method, three of butter and three of oleomargarine, and as the crystals obtained in the two cases are, in some

| No. | Sample.  | Deposit at 17° C.<br>1 cc. | Melting-point.<br>40.3° C. | Microscopic appearance.                                    | Refractometer reading of<br>soluble part.<br>inseparable<br>part. |      |
|-----|--|----------------------------|----------------------------|--|---|------|
|     |  |                            |                            |  | 46.0  | 46.1 |
| 1   | Pure lard .....                                | 4 cc.                      | 43.2° C.                   | beef crystals abundant.                                    |   |      |
| 2   | 90 per cent. lard, No. 1.<br>oleostearin ..... | 10 cc.                     | 44° C.                     | { beef fat crystals.<br>no lard crystals.                  |   |      |
| 3   | 10 " " lard, No. 1 .....                       | 10 cc.                     | 44° C.                     | { no lard crystals.<br>beef fat crystals.                  |   |      |
| 4   | 20 " " oleostearin .....                       | 10 cc.                     | 46° C.                     | { no lard crystals.<br>beef fat crystals.                  |   |      |
| 5   | 70 " " lard, No. 1 .....                       | 18½ cc.                    | 53.5° C.                   | no lard crystals.  |   |      |
| 6   | Oleostearin .....                              | 24 cc. full<br>16 cc.      | 47° C.                     |  | 39.1  | 40.8 |
| 7   | Beef suet .....                                | less than 1 cc.            |                            | { beet crystals abundant.<br>very few small lard crystals. |   | 42.0 |
| 8   | Head fat of hog .....                          | 1½ cc.                     |                            | { very few small lard crystals.<br>beef crystals.          |   | 39.2 |
| 9   | 90 per cent. head fat, No. 7 .....             | 2½ cc.                     |                            | { no lard crystals.  |   |      |
| 10  | 10 " " beef suet .....                         | 3 cc.                      | 52.2° C.                   | splendid crystals.   |   |      |
| 11  | Mutton suet .....                              | 18½ cc.                    |                            | resembling beef crystals.                                  |   |      |
| 12  | 90 per cent. head fat, No. 7 .....             | 1½ cc.                     |                            | { mutton crystals.<br>very few lard crystals.              |   |      |
| 13  | 10 " " mutton suet .....                       | 4 cc.                      |                            | { mutton crystals.<br>no lard crystals.                    |   |      |
| 14  | Pork side fat .....                            | 1 cc.                      | 34° C.                     |  | 44.8  | 45.1 |
| 15  | 87½ per cent. side fat, No. 14 .....           | 4½ cc.                     | 39° C.                     |  | 44.0  | 45.0 |
| 16  | 12½ " " beef suet .....                        | 6 cc.                      | 40.5° C.                   | { beef fat crystals.<br>a few lard crystals.               |   |      |
| 17  | 75 " " side fat, No. 14 .....                  | less than 1 cc.            | 43.5° C.                   |  | 43.9  | 45.0 |
| 18  | 25 " " beef suet .....                         | 1½ cc.                     |                            |  | 44.5  | 45.3 |
| 19  | 90 per cent. pork kidney fat, No. 17 .....     | 4 cc.                      | 45° C.                     | very long lard crystals.                                   |   |      |
| 20  | 10 " " beef suet .....                         | 1½ cc.                     | 39° C.                     |  | 42.5  | 40.0 |
| 21  | Pure lard .....                                | 1 cc.                      | 40.3° C.                   | only lard crystals.  |   |      |
| 22  | Commercial lard .....                          | 4½ cc.                     | 41.5° C.                   | " "  |   |      |
| 23  | " " .....                                      | 3 cc.                      | 40.4° C.                   | " "  |   |      |
| 24  | " " .....                                      | 5 cc.                      | 38.8° C.                   | beef fat crystals.   |   |      |
| 25  | " " .....                                      | 3 cc.                      | 36° C.                     |  |   |      |
| 26  | " " .....                                      | 4 cc.                      | 35° C.                     |  |   |      |
| 27  | Pure lard .....                                | 4 cc.                      |                            |  |   |      |

respects, similar, I do not feel able to make a positive statement in regard to the diagnostic value of this test in all cases. However, the difference in the appearance of the crystals, so far as I have yet observed, seems to be sufficiently great to serve as a means of distinguishing butter from oleomargarine.

From oleomargarine I have obtained perfect crystals of lard and of beef fat. Butter crystals are somewhat lard-like in appearance, but are much shorter and are frequently in rosette clusters.

The refractometer readings given in the table were made with a Zeiss butyrorefractometer. The first column gives the scale reading of the original sample, the second, or part soluble in the fusel oil at 17° C., and the third column, of the insoluble portion. The indices of refraction corresponding to the scale readings of this instrument can be found in Wiley's Agricultural Chemistry.

The fusel oil used in this work had a boiling-point of 129° C. and specific gravity of 0.8159.

## CONTRIBUTIONS TO THE CHEMISTRY OF DIDYMUM.

BY L. M. DENNIS AND E. M. CHAMOT.

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THE announcement by Mosander<sup>1</sup> in 1842 of his discovery of a new element which he found accompanying cerium and lanthanum, and to which he gave the name didymium, was followed by careful and able investigations by Mosander and others upon the chemistry of this obscure group. The information which they obtained by means of purely chemical methods was, however, both meager and contradictory,<sup>2</sup> and it was not until the discovery by Gladstone<sup>3</sup> had put into chemists' hands a new analytical method that the results began to be fairly definite and satisfactory.

The spectroscope affords a means of detecting small amounts of earths yielding absorption spectra, and thus makes possible the preparation of purer compounds of such elements as cerium, lanthanum and yttrium, which give no absorption bands; but the most interesting results of the employment of spectroscopic

<sup>1</sup> *Ann. Chem. Pharm.*, 44, 125.

<sup>2</sup> Hermann: *J. prakt. Chem.*, 34, 182, doubts the existence of didymium.

<sup>3</sup> "On an Optical Test for Didymium," *J. Chem. Soc.*, 10, 219.

methods are seen in the gradual resolution of Mosander's didymium into a number of component earths. Gladstone<sup>1</sup> mentioned only two bands in the absorption spectrum of a didymium solution, while Erdmann<sup>2</sup> mapped seven lines, and said that there might be an eighth in the extreme violet. Rood<sup>3</sup> stated that there are twelve, and Bahr and Bunsen<sup>4</sup> gave measurements of eleven, while later observers<sup>5</sup> describe about twenty bands. These twenty bands which, ten years ago, Krüss and Nilson ascribed to didymium, show that the separation of old didymium into several elements had already begun, for they do not include several bands which had formerly been thought to be due to didymium, but which Boisbaudran<sup>6</sup> in 1878 had shown to be caused by a new element which he had separated and which he named samarium. In 1885 Auer von Welsbach<sup>7</sup> succeeded in separating didymium into two earths, which he called *neodym* and *praseodym*, but which, following the example of Krüss,<sup>8</sup> should be termed *neodidym* and *praseodidym*. These two earths have markedly different properties, the neodidymium giving rose red salts, while those of the praseodidymium are green. There can be little doubt, however, that both are composite and that neither one is an *element* in the present acceptation of that term. Krüss and Nilson,<sup>9</sup> upon examining didymium extracted from many different minerals, found that the same absorption bands varied in relative intensities in the samples of didymium from these various sources, and concluded that our present didymium probably consists of not less than nine elements. Crookes has made the suggestion that each element may yield but one absorption band, and says: "According to this hypothesis, therefore, neodymium and praseodymium must not be considered as actual chemical elements, but only the names given to two groups of molecules into which the complex molecule didym-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *J. prakt. Chem.*, 85, 394.

<sup>3</sup> *Chem. News*, 6, 140.

<sup>4</sup> *Ztschr. anal. Chem.*, 5, 109.

<sup>5</sup> Lecoq de Boisbaudran: Spectres lumineux, Texte, p. 87; Krüss and Nilson: *Ber. d. chem. Ges.*, 20, 2146.

<sup>6</sup> *Compt. rend.*, 89, 212.

<sup>7</sup> *Monatshafte*, 6, 477.

<sup>8</sup> *Ann. Chem. (Liebig)*, 265, 3. Krüss and Nilson ask (*Ber. d. chem. Ges.*, 20, 2166), "Was bedeutet 'dym'?"

<sup>9</sup> *Ber. d. chem. Ges.*, 20, 2166.

ium splits up by one particular method of fractionation."<sup>1</sup> Thompson<sup>2</sup> thinks that the six bands in the blue and violet, having approximately the wave-lengths 482, 476, 469, 462, 444 and 428, are due to at least five different components. Becquerel and others similarly state their belief in the compound nature of didymium.

It would seem natural, then, that having become convinced of the compound character of old didymium, chemists should at once undertake the isolation of the various constituents of this earth. Many of our ablest investigators have endeavored to do this, but the various bases are so closely allied in their chemical characteristics that, up to the present time, only approximate separations have been effected, and these separations have, for the most part, been accomplished by the employment of methods of fractionation that constant use has shown to be capable of giving only imperfect separations, and that at the expenditure of much time and labor. The need, then, at the present time is for new methods of separation or critical examination of the older methods, so that we may be able to obtain sharper results in shorter time. The experimental work described below was undertaken with this end in view, and while we are as yet unable to offer new data concerning the components of didymium, we trust that our observations upon the splitting of didymium may be of interest to workers in this field.

The mixture of earths, which was used for the work, was extracted from monazite sand from Brazil. The sand was decomposed by sulphuric acid and the rare earths were separated from the other elements present by the usual methods. The large amount of cerium which accompanied the other earths was removed by the chlorine method devised by Mosander, as this was found to be more suitable to the treatment of large amounts (we had in hand 9,200 grams of the dry oxalates) than was the fusion of the nitrates with a mixture of sodium and potassium nitrates.<sup>3</sup>

The following procedure was finally adopted : Tall bottles of a capacity of from fifteen to twenty liters, were fitted with two-hole rubber stoppers, one hole carrying a glass tube of about

<sup>1</sup> *Chem. News*, 54, 27.

<sup>2</sup> *Chem. News*, 55, 227.

<sup>3</sup> Dennis and Magee: *This Journal*, 16, 649.

one cm. diameter, reaching to the bottom of the bottle, the other an exit tube ending just below the stopper. The bottles were then connected in series by rubber tubing, so that the chlorine would pass through all of them in turn. Eight to ten liters of the moderately dilute solution of nitrates of the earths was poured into each bottle and a strong solution of potassium hydroxide was then added until the reaction was distinctly alkaline. Each bottle was filled with water to within six inches of the top. Chlorine gas was then led into the first bottle at a rapid rate, any unabsorbed gas passing into the second. By shaking the first bottle from time to time, it was found easy to determine when no further absorption of gas was there taking place. The treatment was then continued a little longer, when the first bottle was removed and the gas passed directly into bottle number two, a fresh bottle being placed at the end of the row. By operating in this way there were always three bottles in line, the last being a fresh one. No loss of chlorine could occur and the operation being continuous, a large amount of material could be treated in a short space of time. After allowing the chlorinated portions to stand until the insoluble ceric hydroxide had settled, the supernatant solution was siphoned off and filtered. The clear solution thus obtained contained the earths of the didymium and yttrium groups free from ceria. This solution was transferred to tall glass cylinders of about twenty liters capacity and the liquid was violently mixed by means of the air blast or a Rabe turbine, oxalic acid, meanwhile, being slowly run in until in excess. The precipitate was allowed to settle, the supernatant liquid was drawn off with a siphon and the cylinder was again filled with distilled water. After each addition of water the contents of the cylinder was stirred for an hour, and the above operation was repeated until the wash-water was free from chlorides. More didymium was separated from the insoluble ceric hydroxide by repeatedly washing the latter with water and then dissolving it in hydrochloric acid, adding potassium hydroxide and chlorinating once more. The chlorine which was used came from a cylinder containing ninety pounds of the liquefied gas. This was found to be cheaper and easier to control than the production of the gas by the usual methods.

The thoroughly washed oxalates of the earths freed from

cerium as above, were dried in an air-bath, ignited in large platinum dishes and dissolved in dilute nitric acid. The clear pink solution showed no trace of cerium when tested with hydrogen peroxide and ammonium hydroxide, and was therefore ready for fractionation, unless it was desired to first remove the earths belonging to the yttrium group. To remove the yttrium group, the solution of the nitrates of the earths was diluted and placed in a tall cylinder whose contents could be rapidly stirred from top to bottom by means of a turbine. Potassium sulphate was added in sufficient quantity to constantly maintain quite a thick layer of the crystals on the bottom. In this way a very satisfactory separation can be accomplished in a far shorter time than by any method with which we are familiar. In the absence of a turbine, almost as good results can be obtained by using a strong air blast, but in this case a quantity of potassium sulphate should be maintained near the surface of the liquid by means of a percolator or similar device.

The precipitate from the above treatment contained the double sulphates of the didymium group. It was washed repeatedly with a saturated solution of potassium sulphate and was finally thrown upon a Witt plate and sucked dry with the suction-pump. The insoluble sulphates were then dissolved in a moderately dilute ammonium acetate solution,<sup>1</sup> filtered, and the clear liquid precipitated with ammonium hydroxide, hydrochloric acid sufficient to decompose the ammonium acetate having first been added. The hydroxides were washed as usual until no further test for sulphate could be obtained by barium chloride. These hydroxides were then dissolved in nitric acid and this solution was used in the subsequent work. In one case in which the yttrium group was removed after a series of fractional crystallizations had been completed, it was found that the double potassium sulphate salts of the earths at the neodidymium end of the series dissolved much more easily in ammonium acetate than did the praseodidymium fractions.

The method of fractionation which was first tried was that of Welsbach,<sup>2</sup> but the details which he gives, especially concerning the strength of acid and the amount of water to be added, are

<sup>1</sup> Urbain: *Bull. Soc. Chim.*, 15, 349, 1896.

<sup>2</sup> *Monatshefte*, 6, 477.

vague and our results when following his directions as closely as possible, were quite unsatisfactory.

It was soon found that the results of the fractionation were greatly influenced by the amount of the nitric acid present. If a large amount of nitric acid is added, the lanthanum double salt separates in the first two or three fractions, and the subsequent splitting of the didymium is then very slow; if, on the other hand, the acid be too weak, a long series of fractions which show but slight differences, is obtained.

The method used by Bettendorff<sup>1</sup> with material high in lanthanum and low in didymium was next tried, but as our oxides contained didymium in excess, the results were again unsatisfactory. It was found, however, that although Bettendorff's method did not produce much effect on the didymium, it appeared to rapidly remove samarium, the absorption bands of this earth being quickly eliminated, whereas the didymium bands showed but little change.

While working upon Bettendorff's scheme of separation, a series of fractions prepared by Welsbach's method had been allowed to stand undisturbed for several days. Upon examining the middle members of this series it was noticed that where the solution had crawled up on the sides of the dishes and crystallized, the crust thus formed was of a deep rose-red color, while the crystals which had formed in the solution were of an entirely different shade of pink. The two kinds of crystals were carefully separated and dissolved in water. The absorption spectra of the two solutions showed that a marked splitting of didymium had taken place, the crystalline crusts which had formed on the sides of the dishes giving a spectrum in which the neodidymium bands were much stronger than those assigned to praseodidymium; there was also a remarkable increase in the intensity of the samarium bands. An aqueous solution of some of the other crystals showed a corresponding increase in the intensity of the praseodidymium bands.

These observations naturally led to the idea that the splitting of didymium might be more rapidly attained by abandoning the customary procedure of concentration by heat and rapid crystallization, and subjecting the solutions to spontaneous evaporation

<sup>1</sup> *Ann. Chem. (Liebig)*, 256, 163.

and slow crystallization. The results exceeded our expectation, for upon making a series of fractions in this manner, very marked spectrum changes were speedily obtained. The sharpness of the separation by slow crystallization is illustrated by the two absorption spectra shown in Plate II. Only the lines in the blue and violet are here mapped, since the changes are greatest in that portion of the field. A portion of the solution containing the double ammonium nitrate was allowed to stand for five days and slowly crystallize. The mother-liquor was then poured off. Its spectrum (II, *a*) shows very strong neodidymium bands, and praseodidymium bands which are relatively much weaker. A saturated solution of the crystals gave the spectrum shown in II, *b*, in which the neodidymium bands are much weaker than those of praseodidymium. The thickness of the solution in each case was ten mm. To test more thoroughly the efficiency of this slow crystallization, somewhat over one kilo of oxides of monazite earths, free from ceria, was converted into double ammonium nitrates, a small amount of nitric acid added, and the whole evaporated to such a concentration that partial crystallization took place only after forty-eight hours. The mother-liquor was then poured off and set aside to crystallize spontaneously. The crystals were dissolved in dilute nitric acid by the aid of heat, and allowed to stand. The crystals and mother-liquor thus obtained were treated as before. After about twenty such fractions had been formed, all those of about the same color, shade, and intensity were united and each portion thus formed was then fractioned separately, similar fractions being from time to time united so as to form a long unbroken series. This process was continued until a series of 105 fractions of the double nitrates had been obtained.

It was found that while the greater part of the lanthanum separated in the first few portions, much of it, contrary to expectation, was carried along to the latter fractions, depositing gradually with the other earths until apparently a certain relative concentration of the different earths was reached, when white crystals again separated, the subsequent fractions becoming more and more intensely pink, until finally the beautiful rose-red salts of the neodidymium and samarium earths were formed. Then suddenly light-colored crystals would appear in the suc-

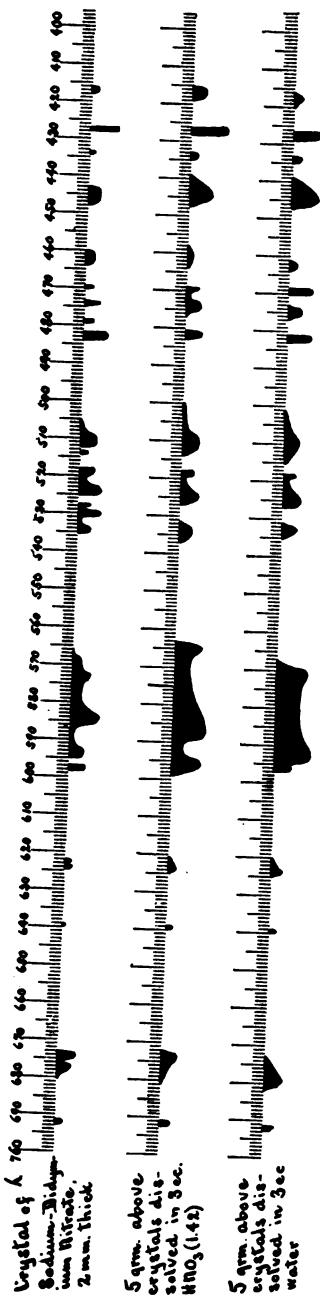
ceeding fractions, and there would again be seen the same series of color changes as had before been observed. For example, fractions 1 to 10 were almost pure lanthanum ammonium nitrate, 11 to 16 showed a growing intensity of the characteristic green tint of the praseodidymium components, 17 was whitish with a tinge of brownish pink, which increased in intensity to 24, 25 had the same tint as 17, but the succeeding fractions up to 29 were decidedly pink, the color growing rapidly darker; 30 showed another falling off to a light color, as did 38, 48, 57, 72, 78, 80, and 88. Above 88 the pink color increased to the end of the series. Throughout the whole series, the spectra of the light-colored crystals, no matter in what portion of the series these lighter crystals had appeared, showed the bands of praseodidymium much more strongly than those of the neodidymium earths, and the samarium bands were generally almost invisible.

Determinations, by the method of Gibbs, of the atomic mass of the earths in the almost colorless fractions gave on the average  $\bar{R} = \text{about } 139$ . Assuming then that these light-colored fractions consisted largely of lanthanum, an examination of the series disclosed the fact that the most marked splitting of didymium was noticeable in fractions but little removed from the light-colored portions, and that the amount of free nitric acid present exerted a powerful influence upon the character of the crystals. It seemed apparent, also, that slow crystallization had been much more effective than the rapid process hitherto employed.

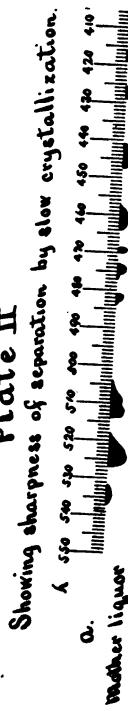
Further experimentation led to the adoption of the following method, which has yielded, on the material from Brazilian monazite, most excellent results:

To a moderately concentrated solution of nitrates of the rare earths, free from ceria and high in lanthana, ammonium nitrate is added in the proportion of four molecules of  $\text{NH}_4\text{NO}_3$  to one of  $\text{R}_2\text{O}$ , where  $\bar{R}$  can be assumed to have a mean atomic mass of 142. Sufficient nitric acid (sp. gr. 1.42) is then added to the solution so as to have one part of acid to four parts of water, by volume. The solution, after thorough stirring, is then evaporated to such a point that nearly all the salts will crystallize out in from twenty-four to thirty-six hours. The small amount of

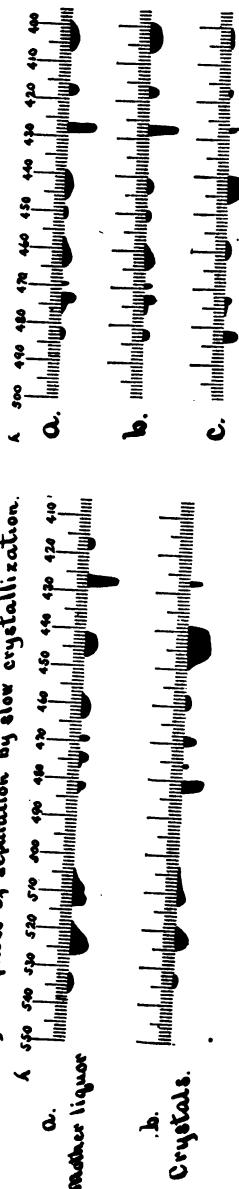
## Plate I.

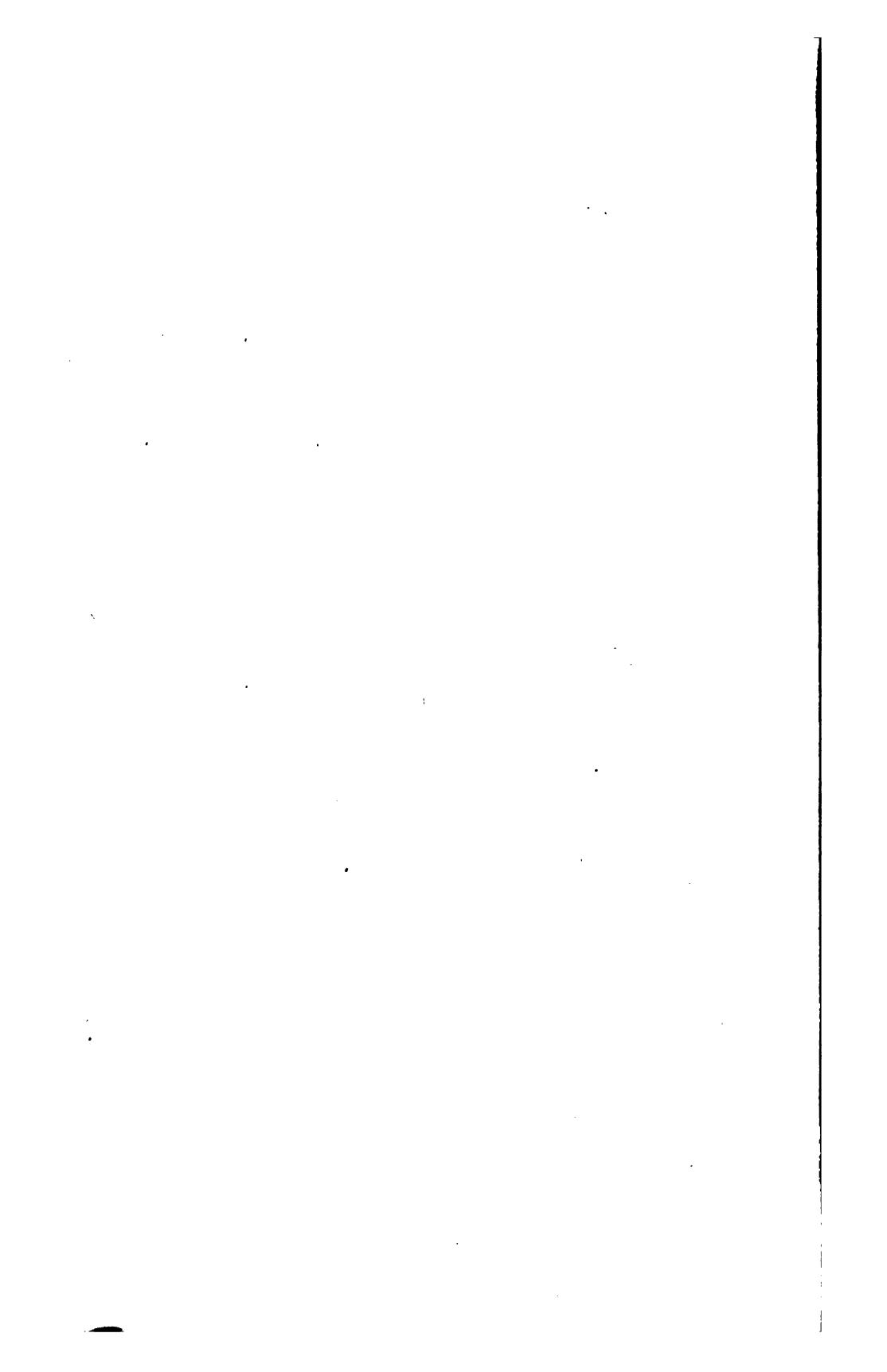


## Plate II



## Plate III





mother-liquor is then set aside and allowed to stand undisturbed until a good crop of crystals has formed ; the mother-liquor from this fraction is poured off and allowed to crystallize spontaneously as before. The large crop of crystals from the original solution is dissolved with the aid of gentle heat, in such an amount of moderately dilute nitric acid ( $1:4$ ) that crystals begin to form in from five to ten hours. After a large proportion of the salts of the earths has separated, the mother-liquor is poured off and allowed to crystallize spontaneously. The crystals are dissolved as before in  $1:4$  nitric acid. The same treatment is given to all crystals and mother-liquors obtained. From time to time such crystals and mother-liquors, irrespective of their position in the series, whose absorption spectra are approximately similar and whose colors are alike, are united and serve as the starting-point of new series of fractions, which in turn are similarly united. The absorption spectra, of the different fractions should be constantly compared and like fractions united, since the rapidity of the method will depend very largely upon the judgment of the operator in properly uniting the various members of the series. The absorption spectra of the different fractions can easily be observed by reflected light, as they lie in the dishes, it being simply necessary to direct a pocket spectroscope toward them. It should be remembered, however, in comparing these spectra, that the spectrum of a crystal is generally very different from that of its solution.<sup>1</sup>

It is seldom, if ever, necessary to remove the crystals from the dishes in order to sufficiently free them from the mother-liquor ; they form compact masses, and the supernatant solution can be thoroughly removed by simply tipping the evaporating dishes and leaving them in that position for a short time.

As the neodidymium end of the series is approached, lanthanum ammonium nitrate which has been obtained in the first fractions, is added to the fractions, together with a little nitric acid ( $1:4$ ), and the whole is gently heated, thoroughly stirred, and set aside to slowly crystallize. The amount of lanthanum

<sup>1</sup> Several years ago Lawrence Smith and Lecoq de Boisbaudran (*Compt. rend.*, 88, 1167) called attention to the change which is caused in the absorption spectrum of didymium when nitric acid is added to the aqueous solution. Becquerel has described (*Compt. rend.*, 104, 165) the variations in the spectra of the crystalline compounds of didymium. In further illustration of these peculiar phenomena, we have ventured to present the three spectra as shown in Plate I.

salts to be added will, of course, depend upon the volume of the solution and the proportion of didymium earths present.

The above method possesses one serious drawback. The double ammonium nitrates of the didymium earths are extremely deliquescent, and in a moist atmosphere their solutions refuse to crystallize. By carrying on the work during the winter months in dry, steam-heated rooms, however, no difficulty whatever was experienced.

When the work was conducted in a fairly dry atmosphere it was found that more satisfactory results could be obtained by adhering to the use of ammonium nitrate than by changing, for the last series of fractions, to sodium nitrate, as Welsbach suggests. For example, it was found possible to obtain in one month, from 800 grams of the mixed oxides, a sample of praseodidymium, which in a saturated solution ten cm. thick, showed only the faintest traces of the bands ascribed to neodidymium.

The fact that the presence of lanthanum facilitates the separation of these two components of didymium was mentioned by both Welsbach and Bettendorff. Schottländer appears to be the only one who added the lanthanum salt to some of his later fractions, but he seems to have discontinued this addition after a few series of fractions had been prepared.<sup>1</sup>

In our work it was found that whenever lanthanum had been largely removed from the solutions under treatment, crystallization took place only with great difficulty and such solutions, when they did crystallize, gave fractions that differed but little from one another in their absorption spectra. If, however, all of these same fractions were again united and a small amount of lanthanum ammonium nitrate added, an immediate change took place in the absorption bands of the different fractions then obtained. Earths high in praseodidymium separated in the early fractions while the last fractions gave only faint bands of this component. The greater part of the samarium seemed to remain in the last mother-liquor. The results of one such crystallization after the addition of the lanthanum salts are shown in Plate III, *a*, *b*, *c*. *a* shows the spectrum of the fraction before the addition of lanthanum. One hundred and twenty grams of lanthanum ammonium nitrate was then added

<sup>1</sup> *Ber. d. chem. Ges.*, 25, 392.

and the solution allowed to slowly crystallize. *b* gives the spectrum of the mother-liquor from the resulting crystals, showing increase in intensity of the neodidymium and samarium bands; *c* is the spectrum of the solution of the crystals, showing marked weakening of the neodidymium bands, and strengthening of the praseodidymium.

These changes in the absorption bands cannot be due merely to the presence of lanthanum in the solutions, since the effect of such addition was repeatedly tried on different solutions and no changes in the character of the absorption bands could be detected other than a uniform weakening due to dilution. As soon, however, as crystallization began, the crystals and mother-liquor showed differences from the original solution.

In fractioning by this method, it was noticed that the heavy band in the orange was not resolved into the component bands described by Welsbach, even when the remainder of the lines had undergone marked changes, this observation confirming the statement of Crookes that "probably didymium will be found to split up in more than one direction, according to the method adopted."<sup>1</sup> In certain fractions the relative intensities of the bands bore out the observations of previous investigators as to the compound nature of both neodidymium and praseodidymium. Thus in one portion the neodidymium band  $\lambda$ -428 was intense, while the other didymium bands were comparatively faint. We also obtained fractions which showed the band  $\lambda$ -443 much more strongly than any other bands.<sup>2</sup>

CORNELL UNIVERSITY, August, 1897.

## THE TITRATION OF STANNOUS SALTS WITH IODINE.

By S. W. YOUNG.

Received July 31, 1897.

FRESENIUS<sup>3</sup> describes very briefly a method by Lenssen, for titrating stannous chloride with iodine in neutral or faintly alkaline solution. As was pointed out in a previous paper,<sup>4</sup> it was evident that the action of iodine on stannous chloride was a quantitative one also in acid solution. Further study has con-

<sup>1</sup> *Chem. News*, 54, 27.

<sup>2</sup> See also Crookes: *J. Chem. Soc.*, 56, 260.

<sup>3</sup> *Syst. Quant. Chem. Anal.*, 1st Am. Ed., p. 342.

<sup>4</sup> This Journal, 19, 517.

firmed this point, and it has been found perfectly possible to titrate stannous salts with great accuracy in acid solution, provided, of course, there are neither oxidizing or reducing substances also in the solution.

The method of operation is very simple, and consists simply in bringing the stannous salt into solution, preferably with dilute hydrochloric acid, adding starch paste and then standard iodine solution until a blue color is produced. The essential precautions are :

(1) Care to prevent oxidation of the stannous salt solution by undue exposure to air. The solution should be prepared rapidly and titrated immediately.

(2) Since the titration is carried on in acid solution, it is essential that the potassium iodide used in the preparation of the standard iodine solution should be particularly free from iodate, since if this latter were present, it would be decomposed rapidly by the acid in the solution titrated and considerable iodine would be set free from the action of the iodic acid on the potassium iodide. This would, of course, make the results of the titration too low.

As thiosulphate cannot be satisfactorily used in acid solution to titrate against iodine, it will be found very convenient to use a dilute solution of stannous chloride for that purpose. This solution may most conveniently be kept under coal oil, and since its strength changes rapidly even then, its relationship to the iodine solution should be very frequently determined—at least once a day.

The most convenient method for preparing the stannous chloride solution is to treat metallic tin with concentrated hydrochloric acid until the action becomes rather slow. Then filter rapidly through cotton wool, preserving this solution under oil for future use. To prepare from this the dilute solution for titration, the standard of the strong solution is roughly determined, and a portion is then diluted to the desired strength and the standard of this is accurately determined.

In this work the iodine has been first standardized by the usual method with thiosulphate.

Following are the results of determinations made with the method, of the percentage of stannous chloride in the salt

$K_2SnCl_4 \cdot 2H_2O$ , described by Richardson.<sup>1</sup> The agreement of the results is very good. Compared with the theoretical the values run a trifle high (three-tenths to four-tenths per cent.).

The cause of this, it was thought, might lie in the fact that the standardizing of the iodine solution took place under entirely different conditions from those existing in the actual determination, *i. e.*, in neutral instead of acid solution.

In general the standard of iodine by thiosulphate is likely to be a trifle high.

The following method for standardizing was then tried: A fresh solution of stannous chloride was prepared of such strength as to be approximately equivalent to the iodine solution. Portions of C. P. potassium bichromate were weighed out (about two-tenths gram). These were titrated with the stannous chloride solution until the bichromate had been completely reduced and then titrated back with iodine solution until the starch iodine blue was produced. The green color of the chromium chloride does not interfere.

The reaction between potassium bichromate and stannous chloride being

$$K_2Cr_2O_7 + 3SnCl_4 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + SnCl_4$$

and the relationship between the iodine and the stannous chloride solutions being accurately determined, the stannous chloride equivalent of the iodine solution may be calculated. By this method the stannous chloride equivalent was found to be 0.004150 gram per cubic centimeter.

By the thiosulphate method the standard of the same solution had previously been found to be 0.004178 gram per cubic centimeter.

Following are the results of the titration by the thiosulphate standard upon the salt  $K_2SnCl_4 \cdot 2H_2O$ .

|       |       |       |
|-------|-------|-------|
| 50.95 | 50.85 | 51.05 |
| 51.17 | 50.70 | 50.88 |
| 50.87 | 50.88 | ..... |

Following are the same results calculated by the bichromate standard:

|       |       |       |
|-------|-------|-------|
| 50.60 | 50.51 | 50.72 |
| 50.82 | 50.36 | 50.53 |
| 50.52 | 50.53 | ..... |

<sup>1</sup> *Am. Chem. J.*, 14, 91.

The results are in percentages of stannous chloride. The theoretical percentage is 50.49.

The method has the advantage of being less interfered with by the presence of other substances, than is the usual method of titrating with ferric chloride and permanganate. The titrations may be made in the presence of iodides and bromides and in the presence of iron salts, these cases conflicting with the permanganate method.

Although definite data have not yet been obtained, it is believed that the method may be applied in the presence of many organic bodies also.

STANFORD UNIVERSITY,  
July 15, 1897.

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## THE VOLUMETRIC DETERMINATION OF THE NITRO GROUP IN ORGANIC COMPOUNDS.

BY S. W. YOUNG AND R. E. SWAIN.

Received July 31, 1897.

AS was pointed out in the previous paper, "The Titration of Stannous Salts with Iodine," it is possible to accurately determine the amount of stannous tin in a solution by means of standard iodine. This suggested the possibility of determining certain oxidizing agents by utilizing the reducing power of stannous chloride. The following results show that the process is applicable to the determination of the nitro group, at least in dinitrobenzene.

There are requisite for the method :

(1) A standard solution of iodine whose value is accurately known.

(2) A dilute solution of stannous chloride, preferably of such strength that one cc. of it is equivalent to about three cc. of the iodine. The object of using so strong a solution is to avoid the necessity of using too large a volume of it.

The process of determination was as follows :

Weighed samples of pure dinitrobenzene, which had been recrystallized from alcohol, were placed in Erlenmeyer flasks, holding about 500 cc. Ten to fifteen cc. of alcohol were added in order to bring the samples into solution. The relationship between the iodine and stannous chloride solutions was now accurately determined. The flasks were then all connected, in

series, with a Kipp generator for carbon dioxide, and when filled with the gas, the stopper of each was removed, and so much of the stannous chloride solution added as was estimated to be sufficient to reduce the dinitrobenzene and leave a small excess (ten to twenty cc. excess is sufficient). Connection with the gas generator was again established, and a slow stream of the gas was kept passing through the apparatus throughout the process of reduction. The flasks are heated on the water-bath to hasten the process. Under these conditions one and one-half to two hours was found sufficient time to complete the reduction. The addition of twenty to twenty-five cc. of strong hydrochloric acid appeared to hasten the process somewhat.

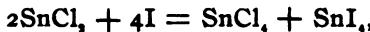
Upon completion of reduction the flasks are removed and the excess of stannous chloride titrated with standard iodine solution, and the net volume of stannous chloride calculated.

The most likely reaction between the nitro group and stannous chloride is as follows :



The results obtained confirm this.

The reaction between iodine and stannous chloride being



it follows that a factor can be found which will be the nitro equivalent of the iodine solution. Then knowing the relationship between the iodine and stannous chloride, we can calculate the volume of iodine equivalent to the volume of stannous chloride used, then from the nitro equivalent of the iodine we can easily calculate the percentage of nitro group in the body. The nitro factor of the stannous chloride might, of course, be determined, but would not be so satisfactory as that of the iodine, on account of the rapidity with which the stannous chloride changes.

Following are eight selected results of the determinations upon dinitrobenzene :

|       |       |
|-------|-------|
| 54.68 | 54.83 |
| 54.51 | 54.64 |
| 54.76 | 54.66 |
| 54.94 | 54.92 |

The theoretical percentage is 54.76.

Following are eight results obtained from *one series* of deter-

minations, no results being omitted. These show the reliability of the method :

|       |       |
|-------|-------|
| 54.63 | 54.44 |
| 54.48 | 54.49 |
| 54.61 | 54.44 |
| 54.40 | 54.44 |

With careful work the method presents no particular difficulty.

Of course it does not follow from the foregoing that the method is very generally applicable to nitro bodies. Investigations will be made to determine the limits of its utility.

STANFORD UNIVERSITY,  
July 20, 1897.

### A MODIFIED METHOD OF FINE SILVER ASSAY.

By AUGUSTUS E. KNORR.

Received August 23, 1897.

In the government assay offices and in the laboratories of silver refineries the assay of fine silver is usually performed according to the method of Gay-Lussac. Two solutions are required, a standard solution of sodium chloride, 100 cc. of which will very nearly precipitate one gram of pure silver, and a second solution, the exact decimal of the former, by means of which the titration is carried to an end. The quantity of fine silver weighed for assay is so adjusted that it will contain one or two milligrams over one gram of pure silver, a preliminary fine assay being made, if necessary, in order to determine the exact quantity to be taken. It is dissolved in nitric acid, 100 cc. of the standard solution of salt are added, and by vigorous shaking the precipitate is caused to collect. In the clear solution the excess of silver is precipitated by means of the decimal solution, added one cc. at a time, and shaken before each addition, in order to observe the cloudiness produced. Fractions of one cc. are estimated by the depth of cloudiness on the last addition of decimal solution causing a perceptible precipitation.

This tentative method, though accurate, is apt to be tedious, much time being consumed if the fineness of the silver is not known within 0.002 to 0.003. About three minutes shaking is required in order to obtain a perfectly clear solution, which is very irksome if there is no mechanical agitator at the operator's disposal.

I have for some time used a modification of this method, largely obviating the shaking, and have found it both speedy and accurate. Instead of making the final titration with the decimal solution of sodium chloride, I prefer to titrate out with potassium thiocyanate according to the method of Volhard, using a ferric salt as an indicator. The standard solution employed is the same as in the original method, variations due to temperature and evaporation being eliminated by running a proof of pure silver with each daily set of assays. The solution of potassium thiocyanate is not an exact decimal of the first, but is standardized against pure silver so that one cc. will precipitate exactly one milligram of silver. A correction for this solution is not required, since in this dilution possible variations would fall beyond the limit of accuracy, which I place at 0.2 to 0.3 milligram. Results are stated in milligrams of silver per thousand.

In performing the assay exactly one gram of the sample is weighed into a well annealed bottle (eight ounce) fitted with an accurately ground stopper; nitric acid, diluted with about two volumes of water free from chlorine, is added, and solution hastened by placing on a hot iron plate. Heating should be continued until the last traces of nitrous acid have been expelled, which would otherwise interfere with the accuracy of the method. Two proofs of pure silver are weighed and dissolved in the same manner; it is not necessary to weigh an exact gram, but the actual weight taken should be accurately ascertained.

When the nitrous fumes have disappeared, enough water is added to prevent crystallizing of the silver nitrate, and 100 cc. of standard salt solution, delivered with great accuracy from an automatic pipette, is run into each assay. The stopper is inserted and the solution shaken until the silver has collected, when it is filtered, five cc. of a solution of ferric ammonic alum added, and the thiocyanate solution run in from a burette until the characteristic color of ferric thiocyanate no longer disappears. This titration should be performed in the cold.

Suppose, for instance, that 1001.3 milligrams of pure silver had been taken for a proof and eight and four-tenths cc. of thio-

cyanate (equal to eight and four-tenths milligrams silver) had been required, then the titer of the salt solution is

$$1001.3 - 8.4 = 992.9.$$

The standard of the salt solution having thus been obtained from the average of two proofs, the fineness of the assays is found by adding the number of cubic centimeters of thiocyanate solution required to the standard found.

Copper and other impurities liable to be found in fine silver do not interfere with the accuracy of this method. It is necessary to separate the silver chloride by filtration because it slowly decomposes silver thiocyanate, and the wash-water must be free from chlorine.

I have repeatedly tested this method and found it accurate, as shown by the following data taken at random from my note book :

|                    | Milligrams<br>taken. | Thiocy-<br>anate.<br>cc. | Standard.            | Thiocy-<br>anate.<br>cc. | Milligrams<br>found. | Differ-<br>ence. |
|--------------------|----------------------|--------------------------|----------------------|--------------------------|----------------------|------------------|
| Proof .....        | 1000.0               | — 8.5                    | = 991.5              |                          |                      |                  |
|                    | 1000.0               | — 8.5                    | = 991.5              |                          |                      |                  |
|                    |                      |                          |                      | Average, 991.5           |                      |                  |
| Fine silver taken. | 996.7                |                          | 991.5 + 5.3 = 996.8  |                          | + 0.1                |                  |
|                    | 996.9                |                          | 991.5 + 5.2 = 996.7  |                          | - 0.2                |                  |
|                    | 998.9                |                          | 991.5 + 7.5 = 999.0  |                          | + 0.1                |                  |
| Proof .....        | 1000.0               | — 7.0                    | = 993.0              |                          |                      |                  |
|                    | 1000.4               | — 7.5                    | = 992.9              |                          |                      |                  |
|                    |                      |                          |                      | Average, 993.0           |                      |                  |
| Fine silver taken. | 994.0                |                          | 993.0 + 1.0 = 994.0  |                          | ..                   |                  |
|                    | 997.0                |                          | 993.0 + 4.2 = 997.2  |                          | + 0.2                |                  |
|                    | 999.0                |                          | 993.0 + 6.3 = 999.3  |                          | + 0.3                |                  |
| Proof .....        | 1000.0               | — 8.2                    | = 991.8              |                          |                      |                  |
|                    | 1000.0               | — 8.0                    | = 992.0              |                          |                      |                  |
|                    |                      |                          |                      | Average, 991.9           |                      |                  |
| Fine silver taken. | 998.0                |                          | 991.9 + 5.9 = 997.8  |                          | - 0.2                |                  |
|                    | 1001.8               |                          | 991.9 + 9.8 = 1001.7 |                          | - 0.1                |                  |

## SOME NEW FORMS OF APPARATUS.

BY AUGUSTUS H. KNORR.

Received August 23, 1897.

### I. AN AUTOMATIC FILTERING SIPHON.

In order to avoid the constant attention required in filtering large bulk's of liquids, the following device has been found useful and an improvement on Mariotte's bottle. In using the latter any sediment or precipitate will go into the filter first and greatly retard the operation. The siphon consists of a glass tube bent after the usual fashion, as shown in Fig. 1, *a*, and it is adjustable by means of a wire support laid over the top of the beaker or vessel containing the solution to be filtered. The longer limb is slightly expanded at the end and a conical valve ground in; the valve has a ball blown on and a knob at the opposite end of the stem, which prevents it from falling out of the tube having a constriction to engage the knob (shown in Fig. 1, *b*). The glass bulb causes the valve to float on the liquid in the funnel, rising as it fills until the valve is pressed home, when the supply of liquid is interrupted, only to admit a fresh quantity when the level again falls. The wire support and manner of placing it on the beaker is shown in Fig. 1, *c*. It is made of two pieces of stout wire twisted about a piece of brass tubing one inch long and fastened with a drop of solder. A short piece of rubber tubing slipped over this allows the shorter limb of the siphon to be adjusted by sliding up or down. Large bulk's of solutions can be filtered through small filters, which is often desirable when there is only a small precipitate, and the latter is left undisturbed until nearly the entire solution has been filtered. A suction-pump can be employed at the same time if desired.

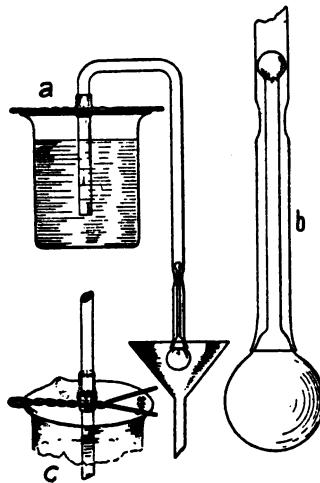


FIG. 1.

This device can be equally well employed in evaporating large quantities of water, and dishes down to the smallest size can be used, which is often an advantage, for instance, in water analysis; when once put in operation it can be left over night with perfect safety.

The operation, filtration, or evaporation having been completed, the siphon is washed out by removing the tip from a wash-bottle and blowing a stream of water through the shorter limb.

## 2. A NEW FORM OF GAS GENERATOR.

The gas generator here described has been found a source of great comfort in metallurgical work, where as in the analysis of refined copper it is not an infrequent occurrence to precipitate fifty to 100 grams of metal at a time in the form of sulphide. Fig. 2 represents the apparatus in its simplest form. The iron sulphide is contained in a calcium chloride jar and is decomposed by allowing hydrochloric acid, diluted with its own bulk of water, to trickle over it drop by drop. The spent acid collects at the bottom, and reaching the level of the U-shaped siphon, it will run out as fast as supplied. It may be discharged directly into the sewer, or a large bottle may be placed under the overflow, to be emptied from time to time. The siphon tube is the novel and essential feature of the apparatus, allowing no spent acid to foul the iron sulphide, while at the same time forming a perfect hydraulic seal against any escape of gas. It must be made sufficiently long for the column of liquor contained in it to overcome the pressure of the liquor in any precipitating vessel of ordinary size. For the same reason the stem of the acid bulb must be at least six or eight inches long.

Fig. 3 shows a larger and somewhat more elaborate form of this generator made for the special purpose of supply-

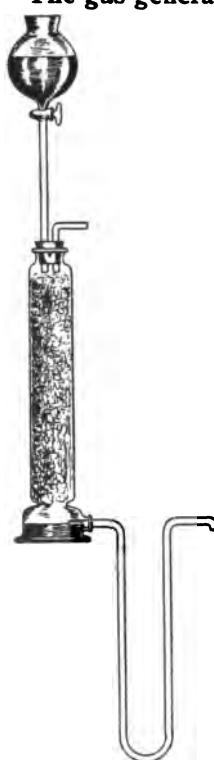


FIG. 2.

ing very large quantities of hydrogen sulphide, where the smaller apparatus would require refilling every day or two. A large druggist's percolator of heavy glass, holding twenty or thirty pounds of iron sulphide was fitted into a calcium chloride jar, acting as a support and at the same time forming one limb of the siphon. The other limb was made of glass tubing appropriately bent. In order to avoid an inconvenient length of the stem of the acid bulb, the top of the latter was made to communicate with the interior of the generator through a T in the delivery tube and proper rubber connections. This equalizes the pressure above and below the acid and allows it to fall by its own gravity. In an apparatus of this size the flow of acid does not immediately answer changes in the speed of acid supply. In order to regulate it, it was found convenient to observe the flow of acid through a small bulb blown on just below the stop-cock and containing a projecting nipple, because after a short time the glass of the generator becomes covered with a black coating through which it is impossible to observe the drops of acid. The top of the percolator was closed with a six-inch rubber stopper permanently sealed in, while the stem of the acid bulb passed through a second rubber stopper, one inch in diameter, fitted into the first. In filling the apparatus only the small stopper is removed, and it was found advisable to use only coarse pieces of sulphide, powder and finer particles having a tendency to wash down and choke the throat of the percolator in a short time. A large acid reservoir placed on a shelf above the acid bulb is a convenience but not a necessity. The whole apparatus was securely clamped against the outside of the hood,



FIG. 3.

only the delivery tube projecting into the same. This generator in daily and almost constant use has been found to work without refilling or other attention for three months at a time, and would perhaps be best appreciated in college laboratories and others requiring an abundant and reliable supply of hydrogen sulphide. It can also be advantageously employed for generating carbon dioxide, hydrogen, and other gases.

### A STUDY OF THE MIXED HALIDES AND HALO-THIO-CYANATES OF LEAD.

BY CHARLES H. HERTY AND T. R. BOGGS.

Received August 24, 1897.

IT has recently been shown<sup>1</sup> by one of us (Herty) that the so-called compound  $\text{Pb} \begin{cases} \text{I} \\ \text{Cl} \end{cases}$  is not a true chemical compound, but a mixture of lead chloride and lead iodide. More recently Herty and Smith<sup>2</sup> have confirmed McMurtry's<sup>3</sup> observation that the substance  $\text{Hg} \begin{cases} \text{Cl} \\ \text{CNS} \end{cases}$  is a true chemical compound, and not a mixture of mercuric chloride and mercuric thiocyanate. This suggested the question, Is the formation of mixed crystals in the one case and a true chemical compound in the other due to the character of the metal present or to the difference in the character of the negative radicals present in each case? To determine this a systematic investigation of the products formed by dissolving lead chloride and lead thiocyanate was undertaken. It has been found that  $\text{Pb} \begin{cases} \text{Cl} \\ \text{CNS} \end{cases}$  is a true chemical compound, just as in the case of  $\text{Hg} \begin{cases} \text{Cl} \\ \text{CNS} \end{cases}$ . Plainly, the character of the metal present is not the determining factor. If then, the difference be due to the character of the negative radicals present, the so-called salt  $\text{Hg} \begin{cases} \text{I} \\ \text{Cl} \end{cases}$  should be a mixture and not a true chemical compound.

However, before beginning work on this point, it has been deemed advisable to make a thorough study of the compounds of lead with the halogens and with thiocyanogen, including all

<sup>1</sup> *Am. Chem. J.*, 18, 293.

<sup>2</sup> *This Journal*, 18, 906.

<sup>3</sup> *J. Chem. Soc.*, 1889, 50.

possible combinations of these. In this way the following have been studied:

|                                  |
|----------------------------------|
| Lead chloride with lead bromide. |
| " " " iodide.                    |
| " bromide " " "                  |
| " chloride " " thiocyanate.      |
| " bromide " " "                  |
| " iodide " " "                   |

In each case seven solutions in water have been prepared, all containing the same weight of lead, but varying proportions of the acid radicals. The middle solution in each series contained the salts in centi-molecular proportions. In the other members of each series arbitrarily taken quantities of one substance were replaced by equivalent quantities of the other substance.

The hot solutions were allowed to crystallize and the crystals thus obtained were dried by pressing between folds of drying paper. The mother-liquors from the first crops were evaporated to two-thirds original volume, and a second crop of crystals obtained. Finally the mother-liquors from the second crops were allowed to evaporate to dryness spontaneously, giving thus a third crop of crystals. Each crop was carefully examined with the microscope to determine its homogeneity. The work is as yet incomplete, but sufficient results have been obtained to justify a description of the work to date.

#### I. LEAD CHLORIDE AND LEAD BROMIDE.

These two compounds are isomorphous, and we would naturally expect mixtures containing varying proportions of the ingredients. Such have been found. The effect of light upon these crystal masses is worthy of note. Wells<sup>1</sup> and Norris<sup>2</sup> have already called attention to the fact that lead bromide is darkened on exposure to light. So in these mixed crystals, this property of lead bromide is retained, the amount of darkening depending on the proportion of lead bromide in the mixed crystal.

#### II. LEAD BROMIDE AND LEAD IODIDE.

Only four solutions were here prepared, beginning with the

<sup>1</sup> *Am. J. Sci.*, 45, 134.

<sup>2</sup> *Am. Chem. J.*, 17, 189.

centi-molecular proportion and replacing portions of lead iodide by equivalent quantities of lead bromide.

In each case crystals of lead iodide alone separated as the first crop, even where the proportion of lead bromide to lead iodide was three and one-half grams to two-tenths gram.

The second crops of crystals, however, were prismatic, resembling, somewhat, lead bromide. These crystals show the presence of both bromine and iodine. The color of the respective crops varies from a greenish-yellow to a light sulphur-yellow. All are darkened by exposure to light. The crops are homogeneous. While no analyses have yet been made it is evident that these crystals are mixtures of lead bromide and lead iodide, in which the lead bromide is largely in excess.

Further, a crystal of lead iodide placed in a cold saturated solution of lead bromide is very gradually changed as the solution evaporates spontaneously and finally disappears, the mass being composed, at dryness, of prismatic, faint yellow crystals. This shows the ability of lead iodide to mix in very small quantities with lead bromide.

### III. LEAD CHLORIDE AND LEAD IODIDE.

Results already published show that these two substances form mixed crystals, but with lead chloride always present in excess. Engelhardt<sup>1</sup> has also shown that lead iodide and lead chloride can form mixed crystals.

A crystal of lead iodide placed in a cold saturated solution of lead chloride begins to change almost immediately. Examined under a microscope the bright yellow hexagonal plate is seen to grow dark, and soon the crystal is seen to break into prismatic crystals of very slight color.

This can be shown on a larger scale by dissolving three and one-half grams lead chloride and 2.4869 grams lead iodide in 350 cc. hot water. On cooling, crystals of lead iodide separate in large quantities. On standing over night in contact with the mother-liquor all of these crystals are changed to yellowish-green prismatic crystals.

All of the evidence thus far obtained tends to show that lead

<sup>1</sup> *Chem. Centrbl.*, 1855, 817.

iodide and lead chloride will crystallize together, the lead chloride being present in excess.

If we consider such substances as instances of solid solution, the results show that lead iodide dissolves in lead chloride to a greater extent than in lead bromide.

#### IV. LEAD CHLORIDE AND LEAD THIOCYANATE.

A microscopic examination of the twenty-one crops of crystals obtained in this series showed three substances present, either singly or crystallizing singly side by side, lead thiocyanate, lead chloride, and a new salt, the lead chloro-thiocyanate, formed from the solution containing the ingredients present in centimolecular proportions. There is no evidence of the formation of any mixed crystals.

#### V. LEAD BROMIDE AND LEAD THIOCYANATE.

The results in this series are exactly analogous to those obtained in IV. Chemical union takes place between the lead bromide and lead thiocyanate.

#### VI. LEAD IODIDE AND LEAD THIOCYANATE.

In this series no evidence was obtained of the formation either of a chemical compound or of mixed crystals. In every case it was observed that the two original salts crystallized side by side, each retaining all of its properties.

#### SUMMARY.

Lead chloride with lead bromide forms isomorphous mixtures in all proportions.

Lead chloride with lead iodide forms mixed crystals, always excess of lead chloride.

Lead chloride with lead thiocyanate forms a true chemical compound.

Lead bromide with lead chloride forms isomorphous mixtures in all proportions.

Lead bromide with lead iodide forms mixed crystals, always large excess of lead bromide.

Lead bromide with lead thiocyanate forms a true chemical compound.

Lead iodide with lead chloride forms mixed crystals, chloride in excess.

Lead iodide with lead bromide forms mixed crystals, bromide in large excess.

Lead iodide with lead thiocyanate forms neither mixed crystal nor true chemical compound.

Lead thiocyanate with lead chloride forms a true chemical compound.

Lead thiocyanate with lead bromide forms a true chemical compound.

Lead thiocyanate with lead iodide forms neither a compound nor mixed crystals.

These results can be summarized more suggestively thus :

|   |  |  |
|---|--|--|
| $PbCl_2$ and $PbBr_2$ .                       | $PbBr_2$ and $PbI_2$ .                             | $PbCl_2$ and $PbI_2$ .                               |
| Form isomorphous mixtures in all proportions. | Form mixed crystals. The bromide always in excess. | Form mixed crystals. The chloride always in excess.  |
| $PbCl_2$ and $Pb(CNS)_2$ .                    | $PbBr_2$ and $Pb(CNS)_2$ .                         | $PbI_2$ and $Pb(CNS)_2$ .                            |
| Form a true chemical compound.                | Form a true chemical compound.                     | Form neither mixed crystals nor a chemical compound. |

What is the explanation of these phenomena? Several lines of thought suggest themselves :

1. The relative solubilities of the individual substances.
2. The crystal form of the constituents.
3. The electro-potential character of the negative radicals.
4. The amount of dissociation in solution.

It is probable that the explanation is to be found, not alone in any one of the above suggestions, but in several. At the present it is not safe to draw any conclusions or make any generalizations, for there are still a considerable number of facts to be supplied. The work is being carried on as rapidly as possible, and it is hoped soon to have sufficient definite information to throw some light on the question of "chemical compound or mixed crystals."

A series of investigations on mercuric salts is now being carried on in this laboratory analogous to the work on the lead salts. The evidence from this may throw still more light on the question.

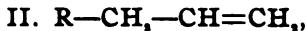
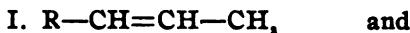
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

## DERIVATIVES OF EUGENOL.

BY F. J. POND AND F. T. BEERS.

Received June 29, 1897.

THE two classes of unsaturated benzene derivatives having the general formulas,

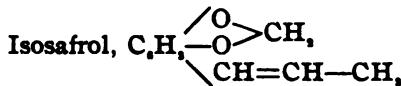
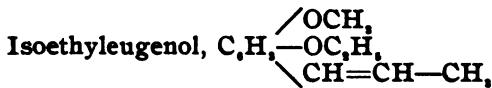
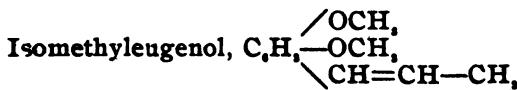
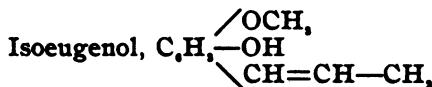


contain the unsaturated group C<sub>3</sub>H<sub>2</sub> joined to a benzene nucleus. In the first class of compounds the C<sub>3</sub>H<sub>2</sub> group has a propenyl, in the second an allyl structure.

The study of these bodies has been especially directed towards finding a suitable reaction by means of which the character of the unsaturated group might be definitely determined.

The results obtained by the action of nitrogen trioxide on anethol, described by P. Toennies,<sup>1</sup> and those of A. Angeli,<sup>2</sup> embracing the action of the same reagent on eugenol, isoeugenol, safrol, isosafrol, apiole, and isoapiole, led Angeli to give the following classification to these bodies:<sup>3</sup>

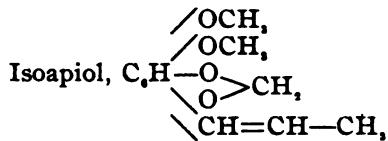
I.



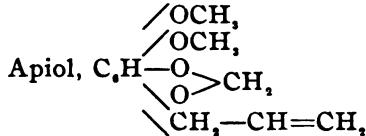
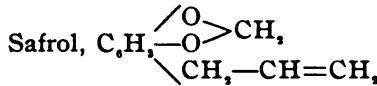
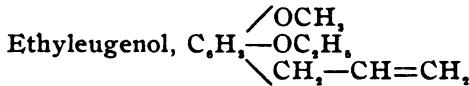
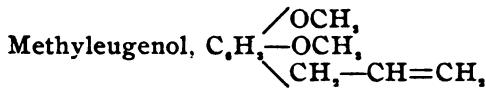
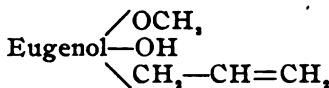
<sup>1</sup> Ber. d. chem. Ges., 22, 1511; 19, 1845; 18, 850; 20, 2982.

<sup>2</sup> Gazz. chim. ital., 23 (II), 445; Ber. d. chem. Ges., 24, 3996.

<sup>3</sup> Ber. d. chem. Ges., 24, 3994.



II.



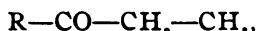
All members of the first group were said to give nitrosites when treated with nitrous anhydride, while those in the second class did not. Hence it was assumed that one of the properties which the compounds with a propenyl side chain possessed was to form these addition-products with nitrogen trioxide, which could not be obtained from the allyl side chain bodies.

Later, however, Angeli<sup>1</sup> was able to prepare similar addition-products from the compounds containing the allyl group, and the reaction therefore could not be called characteristic for the propenyl series.

During the study of the action of sodium alcoholate on the bromine addition-products of these two classes of compounds, Wallach and Pond<sup>2</sup> found that some of the propenyl series gave dibromides, which, on treatment with sodium alcoholate, yielded ketones having the general formula

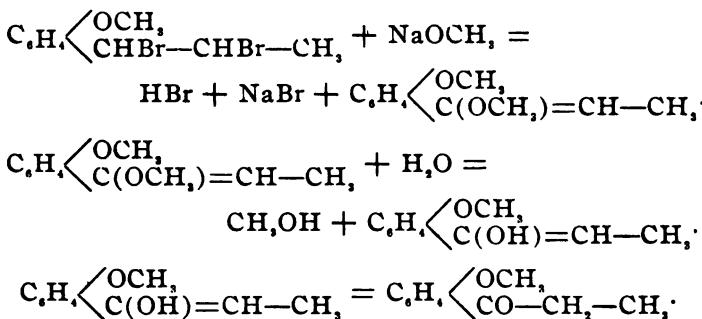
<sup>1</sup> *Ber. d. chem. Ges.*, 26, Ref. 195.

<sup>2</sup> *Ber. d. chem. Ges.*, 28, 2714; also Pond, Inaug. Diss., Goettingen, 1896.



while the bromine products of the corresponding allyl series, treated in precisely the same manner, gave no ketones, but were, partially at least, changed back into the original compounds. This reaction, which was carried out with anethol, safrol, and isosafrol, eugenol and isoethyleugenol, seemed to give reasonable ground for the belief that it might prove a characteristic reaction, by means of which the nature of the side chain in these two classes of unsaturated bodies could be determined.

The formulation of the reaction of sodium methylate on anethol dibromide (anethol being taken as an example of the propenyl compounds) is the following :

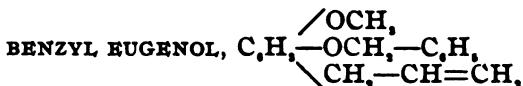


The alcoholate splits off one molecule of hydrobromic acid from the dibromide in the normal manner, while the second bromine atom suffers replacement by the  $\text{OCH}_3$  group. The latter is easily saponified and the resulting unsaturated alcohol, following the Erlenmeyer hypothesis, changes into the more stable saturated ketone.

Eugenol, which was taken as a fair illustration of the allyl series, gave a liquid dibromide, which, on treatment with sodium alcoholate, simply parted with the two bromine atoms, yielding no characteristic body. Safrol acted in much the same manner, while anethol, isosafrol, and isoethyleugenol dibromides gave well defined ketones. It has seemed to us, therefore, of interest to examine this reaction with some other members of the propenyl series, in order, if possible, to give further support to the results already obtained.

Some ester of isoeugenol seemed to promise well for this pur-

pose, and as ethyl and methyl isoeugenol have both shown themselves to conform to the reaction, the question arose whether an aromatic ester of isoeugenol, as for example, benzyl isoeugenol, would not also form a dibromide which could be changed into a ketone. Our results have fully substantiated the belief that such is the case.

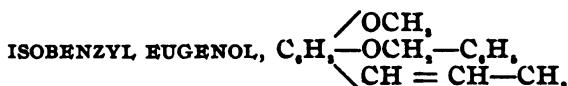


The general rule for preparing esters of eugenol is to treat the potassium or sodium salt of eugenol with an alkyl bromide or chloride.

In such a manner Cahours<sup>1</sup> obtained the benzoyl, toluyl, and ethyl ester, and Wassermann<sup>2</sup> the methyl and some other esters.

Our method was similar to this and consisted in dissolving thirty grams potassium hydroxide in seventy-five cc. alcohol, in a round-bottomed flask with an upright condenser. Seventy cc. eugenol were added and the whole heated on a water-bath. Fifty-three cc. benzyl chloride were introduced, drop by drop, and the heating continued about three hours, until end of the reaction. The potassium chloride formed was dissolved in water and the heavy oil thrown out separated. An attempt to purify by steam distillation proved of no avail, since the oil is almost non-volatile with steam.

The benzyl eugenol is a dark-colored oil, heavier than water, and after drying over calcium chloride boils at about 235° with decomposition. It also suffers decomposition by vacuum distillation.



This propenyl compound was easily prepared from the benzyl eugenol according to the general method of Eykman<sup>3</sup> and Angeli<sup>4</sup> by heating with an alcoholic potassium hydroxide solution.

One hundred and fifty grams potassium hydroxide, 300 cc. alcohol, and seventy-five grams benzyl eugenol were heated on

<sup>1</sup> *Ann. Chem. (Liebig)*, 46, 220; 108, 320.

<sup>2</sup> *Ann. Chem. (Liebig)*, 179, 375.

<sup>3</sup> *Ber. d. chem. Ges.*, 23, 855.

<sup>4</sup> *Gazz. chim. ital.*, 23, (2) 101.

a water-bath for about twenty-four hours. After distilling off most of the alcohol the remaining solution was poured into a liter of water, a heavy oil separating, which, after twelve hours standing, solidified. This was filtered, dried on a porous plate, and crystallized from alcohol. The product is at first rather dark-colored and quite impure, hence repeated treatment with animal charcoal is advisable. The substance has the habit of separating from a saturated alcoholic solution as an oil, which slowly solidifies.

When finally crystallized from alcohol, it is perfectly white and in the form of long, fine needles, melting at 48°.

The analyses gave the following results :

I. 0.1858 gram gave 0.5429 gram carbon dioxide and 0.1113 gram water.

II. 0.1804 gram gave 0.5289 gram carbon dioxide and 0.1113 gram water.

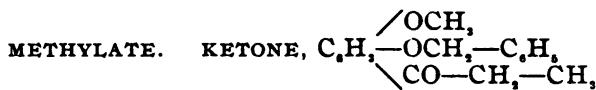
|               | Calculated for<br>$\text{C}_9\text{H}_{10}\text{OCH}_2\text{C}_6\text{H}_5$ | Found. |       |
|---------------|---|--------|-------|
|               |   | I.     | II.   |
| Carbon.....   | 80.31   | 80.13  | 79.94 |
| Hydrogen..... | 7.08  | 6.80   | 6.85  |



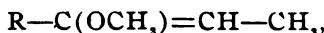
Twenty-five grams isobenzyl eugenol was dissolved in 100 cc. dry ether and after cooling with a mixture of ice and salt, five and four-tenths cc. bromine (one molecule) were added very slowly. The last drops gave the liquid a permanent yellow color, and at the same time a mass of fine white crystals appeared. These were filtered, washed with cold ether to remove excess of bromine, dried, and crystallized from alcohol. A second crop may be obtained from the ether filtrate by washing with a solution of sulphur dioxide to remove bromine, and evaporating the ether. It crystallizes in white needles melting at 122°, easily soluble in alcohol, more difficultly soluble in ether.

No evolution of hydrobromic acid was noticed either during the addition of bromine or on crystallization.

## TREATMENT OF ISOBENZYL EUGENOL DIBROMIDE WITH SODIUM



To a solution of sodium methylate, formed by dissolving five grams of sodium in 100 cc. methyl alcohol, twenty-six grams of isobenzyl eugenol dibromide were added. A violent reaction at once took place with formation of considerable sodium bromide. The solution was heated with an upright cooler, in a water-bath for about three hours. On addition of water a dark-colored, heavy oil separated, which, owing to being difficultly driven over with steam, was removed by a separating funnel. The oil was then boiled for a short time with a dilute solution of potassium hydroxide to insure a complete saponification of the unsaturated ester, *viz.*:



and then allowed to stand twenty-four hours. At the end of this time a solid appeared, and after three days nearly all the oil had changed into the white solid. The latter was filtered by suction, pressed on a plate to remove any adhering oil, and crystallized from ether in small, white needles melting at 93°.

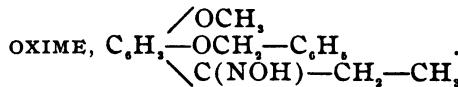
The analyses gave the figures:

I. 0.2282 gram substance gave 0.6306 gram carbon dioxide and 0.1389 gram water.

II. 0.2251 gram substance gave 0.6216 gram carbon dioxide and 0.1354 gram water.

|                | Calculated for<br>$\begin{array}{c} / \text{OCH}_3 \\ \text{C}_6\text{H}_5-\text{OCH}_2-\text{C}_6\text{H}_5 \\ \backslash \text{CO}-\text{CH}_2-\text{CH}_3 \end{array}$ | Found. |       |
|----------------|---|--------|-------|
|                |   | I.     | II.   |
| Carbon .....   | 75.55   | 75.32  | 75.31 |
| Hydrogen ..... | 6.66  | 6.85   | 6.68  |

If the substance actually is a ketone it should naturally be converted into an oxime by treatment with hydroxylamine.



Fifteen grams of the ketone were dissolved in fifty cc. alcohol, heated to boiling, and a hot solution of fifteen grams hydroxylamine hydrochloride in thirty cc. water added. To this solution fifteen grams potassium hydroxide in fifteen cc. water were

slowly added, care being taken to shake well after each addition. On cooling, the whole was poured into ice water, a white, crystalline precipitate being thrown out. After filtering and drying it crystallized from alcohol, yielding beautiful white needles which melt at 118.5°.

Analyses gave the following :

I. 0.1529 gram gave 0.4024 gram carbon dioxide and 0.0886 gram water.

II. 0.1946 gram gave 0.5116 gram carbon dioxide and 0.1120 gram water.

|               | Calculated for   |  | Found. |       |
|---------------|--|--|--------|-------|
|               | $\begin{array}{c} \backslash \\ \text{OCH}_3 \\ \text{C}_6\text{H}_5-\text{OCH}_2-\text{C}_6\text{H}_5 \\ \diagup \\ \text{C}(\text{NOH})-\text{CH}_2-\text{CH}_3 \end{array}$ |  | I.     | II.   |
| Carbon.....   | 71.58  |  | 71.77  | 71.69 |
| Hydrogen..... | 6.66   |  | 6.43   | 6.39  |

There can therefore be no doubt but that the substance obtained from isobenzyl eugenol dibromide by the action of sodium methylate, consists of a ketone mixed with some unsaturated alcohol or ether, the latter being saponified and changed into the ketone structure on heating with potassium hydroxide or with a dilute mineral acid, as was later found to be the case.

The oxime is easily changed back into the ketone melting at 93°, by heating with dilute sulphuric acid.

That the carbonyl group in the ketone occupies the  $\alpha$ - position to the benzene nucleus,

(1)  $\text{R}-\text{CO}-\text{CH}_2-\text{CH}_3$ ,  
and not  $\beta$ .

(2)  $\text{R}-\text{CH}_2-\text{CO}-\text{CH}_3$ ,

has been proved in all this series of ketones by the action of concentrated sulphuric acid on both the ketone and the corresponding oxime, by which propionic acid and not acetic acid results, thus allowing only formula 1.

Isobenzyl eugenol acts thus in a very similar manner to isobethyl eugenol, and adds one more to the list of bodies containing the unsaturated propenyl side chain, whose bromine addition-products may be used as a starting-point for the formation of ketones. It further supports the belief that this reaction may be used to characterize the atomic grouping in the side chain.

Experiments are now under way in this laboratory on eugenol acetic acid and isoeugenol acetic acid, apiole and isoapiole, from which we hope to secure some satisfactory results.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF CINCINNATI.]

### LIII.—ON THE EXISTENCE OF ORTHOSILICIC ACID.

BY T. H. NORTON AND D. M. ROTH.

Received August 27, 1897.

A NUMBER of attempts have been made to ascertain whether silica combined with water to form a sharply-defined meta- or orthosilicic acid, and hitherto the results have been very nearly as fruitless as those undertaken to isolate the corresponding carbonic acids. Nearly all experiments in this field have been in the direction of determining the water remaining in combination with silica after the precipitated hydrate has been kept in an air-bath at 100°, or in a desiccator over dehydrating substances.

Doveri,<sup>1</sup> the pioneer in this subject, found 17 to 17.8 per cent. water in the air-dried powder—source not given. Maschke,<sup>2</sup> using the hydrate precipitated from alkaline silicates by hydrochloric acid, found from 11.6 to 14.4 per cent. Fuchs,<sup>3</sup> Merz<sup>4</sup> and Gottlieb<sup>5</sup> analyzed the hydrate obtained by the action of water on silicon tetrafluoride. Fuchs found 9.3 per cent. water in a sample dried thirty days over sulphuric acid, and 6.75 per cent. in a sample dried eighteen days at 100°. Merz found for the same 8.66 per cent. and 6.31 per cent. respectively. Gottlieb, whose experiments were made with the greatest care, found 6.13 per cent. water after desiccation over sulphuric acid for 131 days and 4.47 per cent. water after desiccation at 100°. His results point to the formulas  $H_4Si_2O_{10}$  and  $H_2Si_2O_8$ . He concludes, "from these few determinations we may say with certainty that the compound known as orthosilicic acid, having the formula  $H_2SiO_4$ , does not exist any more than the so-called metasilicic acid  $H_2SiO_3$ , as the former requires 37.5 per cent., and the latter 23.07 per cent. water, while even an air-dried silicic acid does not contain the latter amount." Rammelsberg<sup>6</sup> says "Gottlieb found 6.13 per cent. water in the acid dried over sulphuric acid, and 4.50 per cent. water in that dried at 100°-140°. I found in the first case, without any special precautions, 4.50 per

<sup>1</sup> *Ann. chim. Phys.*, [3], 21, 40.

<sup>2</sup> *Pogg. Ann.*, 156, 90.

<sup>3</sup> *Ann. chem. (Liebig)*, 8a, 577.

<sup>4</sup> *J. prakt. chem.*, 99, 177.

<sup>5</sup> *J. prakt. chem.*, [2], 6, 185.

<sup>6</sup> *Ber. d. chem. Ges.*, 5, 1007.

cent., in the second 4.00 to 5.00 per cent. water. We accordingly have to deal with hydrates  $n\text{SiO}_4 + \text{H}_2\text{O}$ , where  $n$  lies between four and eight. Air-dried silicic acid, as one may be easily convinced, contains no certain amount of water. In the dry powder is found from thirty-six to thirteen per cent. water. The former amount would indicate the formula  $\text{SiO}_4 + 2\text{Aq}$ , the latter  $2\text{SiO}_4 + \text{Aq}$ . Between these, the figures 23 and 16 per cent. are the most frequent, that is, hydrates  $\text{SiO}_4 + \text{Aq}$  and  $3\text{SiO}_4 + \text{Aq}$ .<sup>1</sup> Other results, equally varying, will be found in the work of Lippert,<sup>2</sup> of Frémy,<sup>3</sup> who used silicon sulphide, of Ebelmen,<sup>4</sup> who used ethyl silicate, Graham,<sup>5</sup> who employed dialysis, Langlois,<sup>6</sup> who used silicon chloride, Fullik,<sup>7</sup> Carnelly and Walker,<sup>8</sup> and Van Bemmelen.<sup>9</sup> The latter made an especially exhaustive study of the hydrates obtained from different sources and dried in air saturated with moisture, claiming that as many as four molecules of water would be held in combination under these circumstances, the powder still being dry to the touch.

In order to decide the question, we devised the following method of isolating the hydrate, which led conclusively to the establishment of the formula  $\text{H}_4\text{SiO}_4$  as representing the composition of silicic acid when freshly precipitated, and rapidly freed from adherent water. This was accomplished briefly by washing the moist hydrate with ether or benzene, and removing the latter by pressure between sheets of bibulous paper.

In detail, the following procedure led to the best results : Silicic acid was precipitated by passing silicon tetrafluoride into water. For obvious reasons this is the simplest method of obtaining the compound free from non-volatile foreign matter. The gelatinous mass was thrown upon a cloth filter, washed with water, and allowed to drain a short time. The water was then removed by successive washings with absolute ether or benzene. Usually 150 to 200 cc. were used in an operation. The washed acid was next wrapped in fine cloth, placed between several thicknesses of heavy filter paper and exposed to strong pressure

<sup>1</sup> *Ann. chim. phys.* [3], 38, 327.

<sup>2</sup> *Ann. chim. phys.* [3], 16, 129.

<sup>3</sup> *Ann. Chem. (Liebig)*, 121, 1.

<sup>4</sup> *Ann. chim. phys.* [3], 52, 331.

<sup>5</sup> *Ber. d. chem. Ges.*, 1898, 2121.

<sup>6</sup> *J. Chem. Soc.*, 53, 81.

<sup>7</sup> *Ber. d. chem. Ges.*, 11, 2232; 13, 1467; *Rec. trav. chim.*, 7, 69.

in a vise. After several changes of the paper, and absorption had apparently ceased, the cloth was changed, and the operation repeated. The cake was then removed from the cloth, enclosed in gray filter-paper and pressed again. (Cloth was necessary at first on account of the adherence of paper to the acid, and at the end ordinary coarse gray filter-paper was less torn than the customary white paper.) At this stage the cake was nearly dry. It was broken up, powdered and pressed between paper and porous tiles several times, until all traces of moisture had disappeared. This point was easily detected by the eye. A portion of the perfectly dry mass, which amounted ordinarily to ten grams at this stage, was transferred to closed watch glasses, and from these weighed off into a platinum crucible. After ignition the amount of silica present and the consequent loss of water, were determined. About forty-five minutes elapsed usually between the beginning of the operation of pressing and the weighing of the sample for analysis. After a little practice it is possible to detect easily the point of disappearance of all moisture, of whatever nature, which is mechanically present. No time is lost at this stage in taking the sample to check the composition, as the loss of chemically combined water begins at once, and its rapidity is dependent only upon prevailing hygroscopic conditions.

The following determinations of orthosilicic acid, as prepared above, were made. Benzene was employed for the washing in Nos. 9, 10, and 11; in all other cases absolute ether was used.  $H_4SiO_4$  should lose, theoretically, 37.5 per cent. of water.

| No.     | Weight of<br>sample.<br>Gram. | Water lost.      |           | Ratio of water<br>to silica. |
|---------|-------------------------------|------------------|-----------|------------------------------|
|         |                               | Weight.<br>Gram. | Per cent. |                              |
| 1.....  | 0.115                         | 0.0428           | 37.30     | 1.97 : 1                     |
| 2.....  | 0.2884                        | 0.1054           | 36.55     | 1.92 : 1                     |
| 3.....  | 0.2826                        | 0.1046           | 37.02     | 1.96 : 1                     |
| 4.....  | 0.1760                        | 0.0660           | 37.50     | 2.00 : 1                     |
| 5.....  | 0.3560                        | 0.1370           | 38.48     | 2.08 : 1                     |
| 6.....  | 0.3642                        | 0.1348           | 37.01     | 1.96 : 1                     |
| 7.....  | 0.2943                        | 0.1098           | 37.31     | 1.98 : 1                     |
| 8.....  | 0.2948                        | 0.1098           | 37.25     | 1.98 : 1                     |
| 9.....  | 0.2473                        | 0.0963           | 36.50     | 1.92 : 1                     |
| 10..... | 0.2368                        | 0.0873           | 36.60     | 1.92 : 1                     |
| 11..... | 0.1497                        | 0.0562           | 37.54     | 2.00 : 1                     |

As was shown by experiment, absolute alcohol could not be used in place of ether or benzene. Its affinity for water is much stronger than that of silicon dioxide, and dehydration began long before the removal of the water mechanically present.

Orthosilicic acid, as obtained above, is an amorphous white powder perfectly dry to the touch, which may be preserved indefinitely in hermetically closed vessels, but loses its water of hydration steadily on exposure to the air, and especially when in contact with absorbent media.

As examples of this latter property the following analyses were made of (A) samples taken from cakes just dried, and (B) of samples taken from the same cakes, after being pressed for five to ten minutes longer between sheets of filter paper.

| No.    | Water.          |                 |
|--------|-----------------|-----------------|
|        | A.<br>Per cent. | B.<br>Per cent. |
| 1..... | 37.02           | 37.01           |
| 2..... | 37.50           | 37.30           |
| 3..... | 38.02           | 34.42           |
| 4..... | 37.01           | 36.95           |
| 5..... | 37.31           | 33.30           |
| 6..... | 36.50           | 36.40           |
| 7..... | 36.60           | 36.10           |
| 8..... | 37.50           | 36.40           |

It is probable that in all our experiments a slight loss of water of hydration occurred before the ether or benzene was completely removed by contact with bibulous paper, as the average of the analytical results is slightly below the theoretical figure, 37.5.

The existence of the orthosilicic acid as a definite body may be therefore considered as established.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF CINCINNATI.]

#### LIV.—DERIVATIVES OF BENZENESULPHONIC ACID.

BY T. H. NORTON.

Received August 27, 1897.

In connection with a general study of the derivatives of benzenesulphonic acid,<sup>1</sup> carried on in this laboratory, the material for the two following notes was collected.

##### PREPARATION OF BENZENESULPHONIC BROMIDE.

The only recorded method of preparing the substance is that

<sup>1</sup> Norton and Schmidt: *Am. Chem. J.*, 10, 136; Norton and Westenhoff: *Ibid.*, 10, 129.

in a vise.  
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tion re-  
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consists in warming together  
benzenesulphonic chloride,  
shorter and simpler method for  
is to determine some of its con-  
ref list, as given in Beilstein's  
bromides thus far known, most  
will be seen that the corresponding  
arably used. Experiment showed  
be obtained by treating dry so-  
phosphorus pentabromide. The  
the solid form or dissolved in car-  
method gave the best yield. In  
sulphonate was well rubbed in a  
bromide. Considerable heat was involved.  
water, the benzenesulphonic bromide,  
out in the form of a heavy liquid, colored  
. It was well washed with water, and  
calcium chloride. Several preparations  
was the yield over one quarter of the

promide is a colorless liquid, frequently  
range, of an oily appearance, with a sharp  
Its specific gravity is 1.693 at 21°. It distils  
with slight decomposition.

Carius' method gave :

|       | Found. | Theory. |
|-------|--------|---------|
| ..... | 35.02  | 36.20   |

#### SULPHONATES OF THE ALKALINE METALS.

these salts are used technically, none of them  
subjected to careful analysis or examination.

*Sodium benzenesulphonate*,  $C_6H_5SO_3Na$ . This salt was prepared  
aqueous solution of sodium carbonate to an aqueous  
benzenesulphonate until the point was ex-  
at which no further precipitate was formed. The  
out the sodium benzenesulphonate was evaporated  
crystallization. It crystallizes in the form of  
hydrinous leaflets. It melts with some decomposi-

(Liebig). 342, 373.

tion at about  $450^{\circ}$ . It is insoluble in ether and benzene, and but slightly soluble in alcohol. It dissolves in 1.75 parts of water at  $30^{\circ}$  and in 0.8 part of boiling water.

*Analysis.*—The salt dried to constant weight over sulphuric acid *in vacuo*, lost no weight on heating to  $135^{\circ}$ .

0.3624 gram of the dried salt gave 0.1423 gram  $\text{Na}_2\text{SO}_4$  = 0.046 gram Na = 12.72 per cent.

|              | Theory. | Found. |
|--------------|---------|--------|
| Sodium ..... | 12.77   | 12.72  |

*Potassium Benzenesulphonate*,  $\text{C}_6\text{H}_5\text{SO}_3\text{K}$ .—This salt was prepared in the same way as the sodium salt, potassium carbonate being used. It crystallizes ordinarily in long, delicate, colorless needles, with a silky luster, united frequently in radiated clusters. Long flat prisms are obtained by very slow evaporation. The salt is anhydrous and melts at about  $408^{\circ}$ . It is insoluble in ether and benzene, and nearly insoluble in alcohol. It dissolves in 0.66 part of water at  $30^{\circ}$ , and in 0.29 part of boiling water.

*Analysis.*—The salt dried to constant weight over sulphuric acid *in vacuo*, lost no weight on heating to  $115^{\circ}$ .

0.2567 gram of the dry salt gave 0.1121 gram potassium sulphate = 0.05 gram potassium = 19.58 per cent.

|                | Theory. | Found. |
|----------------|---------|--------|
| Potassium..... | 19.90   | 19.58  |

*Ammonium Benzenesulphonate*,  $\text{C}_6\text{H}_5\text{SO}_3\text{NH}_4$ .—This salt was prepared in a manner similar to those above described, ammonium sulphate being used in the precipitation of the barium salt. Crystals are obtained with difficulty on account of the deliquescent nature of the salt. When prepared in a vacuum, over sulphuric acid, they show a radial structure with pearly luster, but are poorly defined. The salt begins to decompose at  $236^{\circ}$  and melts at  $256^{\circ}$ . It is soluble in 1.02 parts of cold water and in 0.31 part of boiling water. It dissolves in five and two-tenths parts of cold alcohol and in three and one-tenth parts of boiling alcohol, but is insoluble in ether and benzene.

*Analysis.*—The salt dried over sulphuric acid *in vacuo*, lost no weight at  $105^{\circ}$ .

One-half gram of the dry salt gave by the potassium chlorate

method, 0.652 gram barium sulphate, or 0.0895 gram sulphur = 17.87 per cent.

|              | Theory. | Found. |
|--------------|---------|--------|
| Sulphur..... | 18.28   | 17.87  |

*Lithium Benzenesulphonate*, C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>Li.—This salt was prepared in the same way as the sodium salt, lithium carbonate being used. It crystallizes in stellate groups of delicate, white, anhydrous needles. It melts at a dull red heat. It is soluble in 1.02 parts of water at 30°, and in five-tenths part of boiling water, in one and five-tenths parts of cold alcohol, and in nine-tenths part of boiling alcohol. It is insoluble in ether and benzene.

*Analysis.*—The salt dried over sulphuric acid *in vacuo*, lost no weight at 105°.

0.3032 gram of the dried salt gave 0.1032 gram lithium sulphate, or 0.013 gram lithium = 4.27 per cent.

|              | Theory. | Found. |
|--------------|---------|--------|
| Lithium..... | 4.26    | 4.27   |

I am indebted to H. C. Buell and H. E. Newman for aid in these determinations.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF CINCINNATI ]

#### LV.—ON A SOLUBLE COMPOUND OF HYDRASTINE WITH MONOCALCIUM PHOSPHATE.

By T. H. NORTON AND H. E. NEWMAN.

Received August 27, 1897.

THE following experiments were made in connection with an endeavor to enlarge the number of soluble salts of hydrastine, especial interest attaching to the combination of the alkaloid with a mineral salt of recognized value in medicine.

As is well known, but few salts of hydrastine are readily soluble in water. In our work we made use of monocalcium phosphate, which was carefully purified by prolonged washing with alcohol. A saturated solution of the salt in cold water was prepared by thorough trituration, the phosphate being in excess. On triturating this saturated solution with a large excess of pure hydrastine, a certain amount of the latter would enter into solution, time, as was eventually found, being an important factor.

In order to ascertain the nature of the product obtained, the filtered solution was evaporated either by heat or spontaneously, or in a vacuum. In no case was it possible to detect any trace of crystallization. The solution invariably became syrupy, and finally left an amorphous residue quite similar to rosin in its appearance. This residue was soluble in about ten parts of cold water. A small amount of boiling water would change it into a syrup. Both boiling and cold alcohol dissolved it easily and in about the same proportions. The melting-point was 126°-128°. Although there was no criterion of the purity of the substance it was submitted to analysis. No success followed an attempt to determine the amount of hydrastine present by the use of potassium permanganate, as no definite end reaction could be obtained. Resort was then had to incineration, care being taken to avoid unnecessarily high temperatures in the use of platinum dishes for the purpose. The substance dried *in vacuo* was heated to 105°. The very divergent results obtained showed that there was no fixed percentage of water held by the compound after desiccation *in vacuo*. The product of incineration was white, vitreous calcium metaphosphate.<sup>1</sup> It was in all cases calculated to monocalcium orthophosphate, and the difference was assumed to be hydrastine. Analytical results soon showed that prolonged trituration was necessary to increase the amount of the alkaloid taken into combination by the phosphate. From two-tenths to one-half gram was used in each analysis of the substance dried at 105°. The following analytical data were obtained:

| No. | Time of trituration.  | Monocalcium phosphate. | Hydrastine. |
|-----|-----------------------|------------------------|-------------|
|     |                       | Per cent.              | Per cent.   |
| 1   | 10 minutes            | 44.69                  | 55.31       |
| 2   | 15 "                  | 38.33                  | 61.67       |
| 3   | 5 "                   | 55.70                  | 44.30       |
| 4   | 3 "                   | 57.73                  | 42.27       |
| 5   | 80 hours <sup>2</sup> | 29.00                  | 71.00       |
| 6   | 80 "                  | 28.03                  | 71.97       |
| 7   | 40 "                  | 31.00                  | 69.00       |
| 8   | 50 "                  | 30.43                  | 69.67       |
| 9   | 50 "                  | 28.10                  | 71.90       |
| 10  | 6 weeks               | 28.95                  | 71.05       |

<sup>1</sup> Birnbaum: *Jsb. d. Chem.*, 1871, 281.

<sup>2</sup> In experiments 5-10 the alkaloid and the solution were placed in a corked bottle, and this was introduced into a box provided with paddles and suspended on an axis, which was kept in constant agitation beneath a water tap.

In order to appreciate these figures, let us note the theoretical percentages of the simpler possible combinations of monocalcium phosphate and hydrastine.

- A.  $2\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{C}_{21}\text{H}_{31}\text{NO}_9$ .  
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 = 54.10$  per cent.  
 $\text{C}_{21}\text{H}_{31}\text{NO}_9 = 45.90$  per cent.
- B.  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{C}_{21}\text{H}_{31}\text{NO}_9$ .  
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 = 37.9$  per cent.  
 $\text{C}_{21}\text{H}_{31}\text{NO}_9 = 62.1$  per cent.
- C.  $2\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{C}_{21}\text{H}_{31}\text{NO}_9$ .  
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 = 28.9$  per cent.  
 $\text{C}_{21}\text{H}_{31}\text{NO}_9 = 71.1$  per cent.

It will be seen at once that the apparent limit of the amount of hydrastine which can enter into combination with the phosphate, as shown by analyses 5-10, is practically identical with the percentage of the alkaloid present in the hypothetical salt C, where two molecules of monocalcium phosphate are in combination with three molecules of the alkaloid. In the picrate of hydrastine, one of the few crystalline derivatives, we encounter a combination of equal molecules  $[\text{C}_{21}\text{H}_{31}(\text{NO}_9)_2 \cdot \text{OH} \cdot \text{C}_{21}\text{H}_{31}\text{NO}_9]$ , the amorphous sulphate and chloride ( $\text{C}_{21}\text{H}_{31}\text{NO}_9 \cdot \text{H}_2\text{SO}_4$ ) correspond, however, to the formula B. While the formula C is unsupported by analogy and the aid of crystallization is lacking, the analytical data point strongly towards this as the correct expression for the product obtained by the method described.

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#### TORONTO MEETING OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

THE British Association for the Advancement of Science met in Toronto, August 18-25. Many prominent scientific men from Canada and the United States, as well as from Great Britain, were in attendance.

Professor William Ramsay, of London, was president of the chemical section. His address was on "An Undiscovered Gas." A consideration of the periodic law and of the atomic weights of helium and argon (4 and 40) suggests that there may be another similar element with an atomic weight of about 20. Helium has been subjected to a long series of diffusions by Pro-

fessor Ramsay and Dr. Collie in the endeavor to find such a substance. The gas was by this means separated into a lighter portion with a density of 1.98 and a heavier portion with a density of 2.275 ( $H_2 = 1$ ). The spectroscopic examination showed the presence of argon in the heavier portion, but no evidence of the existence of a new gas could be discovered. Such a negative result cannot, of course, be taken as proof of the nonexistence of the substance sought, and Professor Ramsay very courteously concluded his address by expressing the hope that the prophecy implied in it may find its fulfilment on this side of the ocean.

The papers of most interest presented before the section were the following :

Professor Ramsay described in detail the apparatus used for the diffusion experiments with helium, and described experiments which demonstrated that the apparatus could be successfully used to separate air into two portions, one richer and the other poorer in oxygen, while nitrogen cannot be so separated into a lighter and a heavier portion.

Professor B. Brauner, of Prague, Austria, read an interesting paper on "The Atomic Weight of Thorium" and demonstrated the use of ammonium oxalate in separating thorium from other rare metals.

Professor T. W. Richards, of Harvard University, gave a short account of his recent determinations of the atomic weights of nickel and cobalt, which show the same painstaking care and accuracy which has been attained in his previous work.

Mr. Ramage, of Dublin, presented a paper by Professor W. N. Hartley and himself on the 'Spectroscopic Examination of Minerals and Earths.' The paper was illustrated by the projection of photographs of spectra obtained, chiefly, in the oxyhydrogen flame. They have demonstrated the presence of gallium, indium, thallium, and other rare elements in many samples of iron and of iron ores. The presence of gallium, especially, has also been demonstrated from the spectra of the flames of Bessemer converters.

On Monday, Professor Meslans, an associate of Professor Moissan, of Paris, contributed a "Demonstration of the Preparation and Properties of Fluorine." The gas was prepared by the electroly-

sis of anhydrous hydrofluoric acid containing acid potassium fluoride in a copper vessel surrounded with a freezing mixture. To free the gas from vapors of hydrofluoric acid it was passed through a copper coil surrounded with solid carbon dioxide and alcohol. The action of fluorine on charcoal, silicon, sulphur, iodine, potassium iodide, and on various compounds of carbon was demonstrated.

A paper by Professors Moissan and Dewar on the "Properties of Liquid Fluorine" was also read. The boiling-point is  $-185^{\circ}$  to  $-187^{\circ}$ , the critical temperature  $-118^{\circ}$ , the critical pressure twenty-five atmospheres. The density of the liquid fluorine is 1. The gas liquefies in boiling air but not in boiling oxygen. It is soluble in liquid air.

Professor H. B. Dixon, of Manchester, England, read a paper on "Photographs of Explosion Flames." Photographs were projected of explosion flames as taken on sensitive paper attached to a rapidly moving drum. The photographs demonstrate that mixtures of cyanogen with an excess of oxygen burn at first to carbon monoxide, the temperature being probably above the dissociation temperature of carbon dioxide. The velocity of waves in the incandescent gas from mixtures of cyanogen and oxygen, as shown by the photographs, indicates a temperature of  $3,000^{\circ}$  to  $4,000^{\circ}$ .

Professor J. U. Nef, of Chicago, read a paper on the Chemistry of Methylene. The preparation and remarkable properties of some newly discovered derivatives of methylene were described. Among the most interesting of the new compounds are the derivatives of acetylidene,  $\text{Cl}_2=\text{C}$  and  $\text{CHI}=\text{C}$ . In the latter case the isomer  $\text{CH}=\text{CI}$  has also been prepared and exhibits a very remarkable difference in its properties. Dr. Nef appears to consider the preparation of a gaseous carbon of the formula  $\text{C}=\text{C}$  as possible, though, perhaps, scarcely probable.

On Tuesday morning the chemical section met with the sections for physiology and botany to listen to a paper by Professor Meldola, of London, on the Rationale of Chemical Synthesis. About 300 compounds found in plants and animals have been prepared by synthetical processes in the laboratory. The opinion was expressed that most of these compounds are on what may be called a low level, as compared with the most important com-

pounds which are formed synthetically in vegetable and animal cells. The laboratory processes, too, are, as a rule, radically different from the processes within the living forms, though no one now believes that the chemical forces within the organism differ in any respect from those outside. In the discussion which followed, in which several biologists and chemists took part, it appeared to be the general consensus of opinion that very little real knowledge has thus far been gained in regard to the processes which give rise to the synthesis of starch, proteids, and other similar substances within living organisms, and some of the enormous difficulties which prevent, thus far, the successful study of such problems were pointed out.

On Friday evening Professor W. C. Roberts-Austen, of London, gave a lecture on Canada's Metals. The experimental illustrations were striking, though their connection with the subject-matter of the lecture was remote. Among the more notable demonstrations were instantaneous photographs showing the similar phenomena produced by the fall of a bullet into a basin of milk and of a bullet of gold into a plate of gold, the constancy of temperature during the melting or solidification of gold as shown by a thermoelectric couple and galvanometer, and the melting of copper, chromium, and silver in an electric furnace, the phenomena being made visible to a large audience by reflection on a screen by means of a concave mirror.

Other papers presented before the chemical section were :

Prof. W. W. Andrews: Reform in the Teaching of Chemistry.

Dr. J. Waddell: The Permeability of Elements of Low Atomic Weights to the Roentgen Rays.

Dr. J. H. Gladstone and W. Hibbert: Continuation of Experiments on Chemical Constitution and the Absorption of X-Rays.

Dr. W. J. Russell: On the Action Exerted by Certain Metals on a Photographic Plate.

M. Travers: The Occurrence of Hydrogen in Minerals.

Prof. F. P. Dunnington: Titanic Oxide.

Prof. F. P. Dunnington: Deliquescence and Efflorescence of Certain Salts.

Dr. J. Waddell: Notes on Concentrated Solutions of Lithium and Other Salts.

Prof. Ramsay: Demonstration of the Spectra of Helium and Argon.

W. L. T. Addison: The Formation of Crystals.

E. C. C. Baly: A Compound of Ozone and Mercury.

J. W. Walker: The Interaction of Hydrobromic and Bromic Acids.

F. J. Shutt: The Composition of Canadian Virgin Soils.

W. H. Ellis: Analyses of Some Pre-Carboniferous Coals.

Prof. P. C. Freer: The Constitution of Aliphatic Ketones.

Prof. Henry: The Nitroalcohols.

Dr. A. Lehmann: Formation of a Benzene Ring by Reduction.

Dr. C. A. Kohn: Condensation Products of Aldehydes and Amides.

Dr. Hugh Marshall: A New Form of Bunsen Burner.

Prof. W. C. Roberts-Austen: Molecular Movements in Metals.

Prof. W. W. Andrews: The Plaster of Paris Method in Blow-pipe Analysis.

Dr. W. L. Miller and T. R. Rosebrough: The Vapor-Tensions of Liquid Mixtures.

Dr. C. A. Kohn: The Electrolytic Determination of Copper and Iron in Oysters.

W. A. NOYES.

#### BOOKS RECEIVED.

Some Common Poisonous Plants. By V. K. Chesnut. [Reprinted from the Yearbook of the Department of Agriculture for 1896.] 10 pp. U. S. Department of Agriculture, Division of Botany, Washington, D. C.

Commercial Fertilizers. By H. A. Huston. Special Bulletin, Second Edition. August, 1897. 8 pp. Published by the author. Lafayette, Ind.

Analyses of Manurial Substances and Licensed Fertilizers collected during 1897. Bulletin No. 48, July, 1897. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

Annali del Laboratorio Chemico Centrale Delle Gabelle. Vol. III. Pubblicati da Vittoria Villavecchia. Roma: Tipografia Nazionale di g. Bertero via Umbria. 1897.

Lettera al Prof. S Cannizaro; Sopra alcune sostanze che si ricavano dall'olio di sesamo sulla relazione che esse hanno con la reazione cromatica caratteristica di quest'olio; Sopra la composizione delle farine italiane e sui criteri che valgono a caratterizzarle nel commercio; Sul gelsolino; Contributo allo studio delle analisi dei saponi; Sopra i petroli da illuminazione che si consumano in Italia; Sopra la dulcina o parafenetol-carbamide e sul modo di riconoscerla; Sull'analisi dei canditi; Sopra la composizione chimica di alcuni vini greci; Ricerche sui dégras; Sulla determinazione della glicerina nei vini dolci.

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THE SOLUBILITY OF STANNOUS IODIDE IN WATER AND  
IN SOLUTIONS OF HYDRIODIC ACID.

BY S. W. YOUNG.

Received July 31, 1897.

THE following experiments have been made in order to determine the solubility of stannous iodide in water and in different strengths of hydriodic acid at different temperatures.

The stannous iodide used was prepared by the action of hydriodic acid on tin. The hot saturated solutions thus obtained were cooled and the separated crystals of stannous iodide were filtered off by suction, dried on bibulous paper for a few minutes, and then transferred to a large test-tube and shaken repeatedly with carbon bisulphide in order to dissolve out the stannic iodide which is always present. The product was kept under carbon bisulphide in tightly stoppered tubes until wanted.

The hydriodic acid used was prepared by the action of hydrogen sulphide on iodine and water. It was found convenient in preparing an acid of given strength to weigh out the requisite amounts of water and iodine and allow the hydrogen sulphide to act on them. It is possible in this way to prepare acids of any strength with very considerable accuracy. For instance, in one case it was desired to make an acid of thirty per cent. After the acid was prepared analyses gave 29.93 per cent. and 29.97 per cent.

The method used in determining the solubility was as follows:

The requisite solvent and stannous iodide were placed in a large 100 cc. test-tube, which was closed by a stopper with three holes, one for a thermometer reading to tenths, one for a stirrer, and one for the introduction of a pipette for removing the samples. A layer of coal oil about one inch deep was placed upon the solution to prevent oxidation. The whole was heated nearly to boiling for a few moments and stirred constantly to insure saturation. The whole was then supported in a large beaker of boiling water. When the thermometer had remained constant for some time a weighing pipette was introduced and a sample withdrawn, weighed, and the amount of stannous salt determined by titration with standard iodine solution, according to the method described in a previous paper.<sup>1</sup>

In withdrawing the sample in the pipette it was necessary that the solution should be filtered to avoid drawing out more or less solid stannous iodide. This was accomplished by affixing to the tip of the pipette a short piece of rubber tubing, in which was placed a wad of absorbent cotton. The solution, after passing through this filter, was perfectly clear.

Following are the results of two series of determinations of the solubility of stannous iodide in pure water:

| Series 1. |      | Series 2. |      |
|-----------|------|-----------|------|
| T.        | P.   | T.        | P.   |
| 98.5      | 3.43 | 97.3      | 3.70 |
| 84.9      | 3.05 | 87.4      | 3.24 |
| 73.9      | 2.56 | 77.6      | 2.75 |
| 60.1      | 2.09 | 67.5      | 2.34 |
| 51.5      | 1.79 | 59.7      | 2.03 |
| 41.0      | 1.50 | 49.5      | 1.72 |
| 30.5      | 1.21 | 39.4      | 1.38 |
| 20.8      | 1.03 | 29.6      | 1.11 |
|           |      | 19.8      | 0.96 |

T = Temperature.

P = Parts stannous iodide in 100 of solution.

The two series show very good agreement with the exception of the first numbers, the second series having a value of 3.70 parts soluble at 97.3°, while the first series shows only 3.43 parts at 98.5°. This is undoubtedly due to incomplete saturation in the first series. This is indicated by the fact that the curves plotted from the data are more nearly normal with the higher value. The same thing was noticed in some other series.

<sup>1</sup> This Journal, 19, 809.

In Table I, following, are the results of eight series of determinations of the solubility of stannous iodide, in solutions of hydriodic acid, varying in strength from five to thirty-seven per cent. Some of the numbers are averages of duplicates, while some are single determinations. A few experiments showed the method of determination to be very reliable and it seemed probable that the error introduced by oxidation on standing sufficiently long for two parallel determinations to be made, would be greater than any error introduced by the method.

Two peculiarities are immediately noticeable from a study of these data. The first one is that the presence of hydriodic acid up to above fifteen per cent. renders the stannous iodide less soluble than in pure water. In order to show more clearly the nature of this effect the following series of experiments was made :

Solutions of hydriodic acid varying from three to fifteen per cent. were prepared by taking strong acid of known strength and diluting with the calculated amounts of water. These were saturated with stannous iodide by warming and allowed to cool to  $23.5^{\circ}$  C., at which temperature they were allowed to stand for some time with frequent stirring, in order to insure equilibrium. Portions were taken out from each in a weighing pipette and titrated. Following are the results. They cannot lay claim to extreme accuracy, owing to the rather large probable error introduced by the method of making up the dilute acids used :

| Strength of acid.<br>Per cent. | P.1  | Strength of acid.<br>Per cent. | P.   |
|--------------------------------|------|--------------------------------|------|
| 0                              | 1.00 | 9                              | 0.21 |
| 3                              | 0.26 | 10                             | 0.26 |
| 4                              | 0.22 | 11                             | 0.30 |
| 5                              | 0.19 | 12                             | 0.45 |
| 6                              | 0.16 | 13                             | 0.58 |
| 7                              | 0.16 | 14                             | 0.62 |
| 8                              | 0.17 | 15                             | 0.81 |

P = Parts of stannous iodide in one hundred of solution.

These results show that the solubility of stannous iodide decreases with the increase in concentration of the hydriodic acid up to between six and seven per cent., and thereafter increases. The decrease in solubility reminds one of the conduct of common salt and hydrochloric acid. The later increas-

TABLE I.  
SHOWING SOLUBILITY OF STANNOUS IODIDE IN SOLUTIONS OF HYDRIODIC ACID OF DIFFERENT CONCENTRATIONS.

### Temperature.

1 P = Parts stannous iodide in one hundred of solution.

ing solubility would seem to indicate the introduction of a new system in about seven per cent. concentration of hydriodic acid. The nature of this new system will be discussed later.

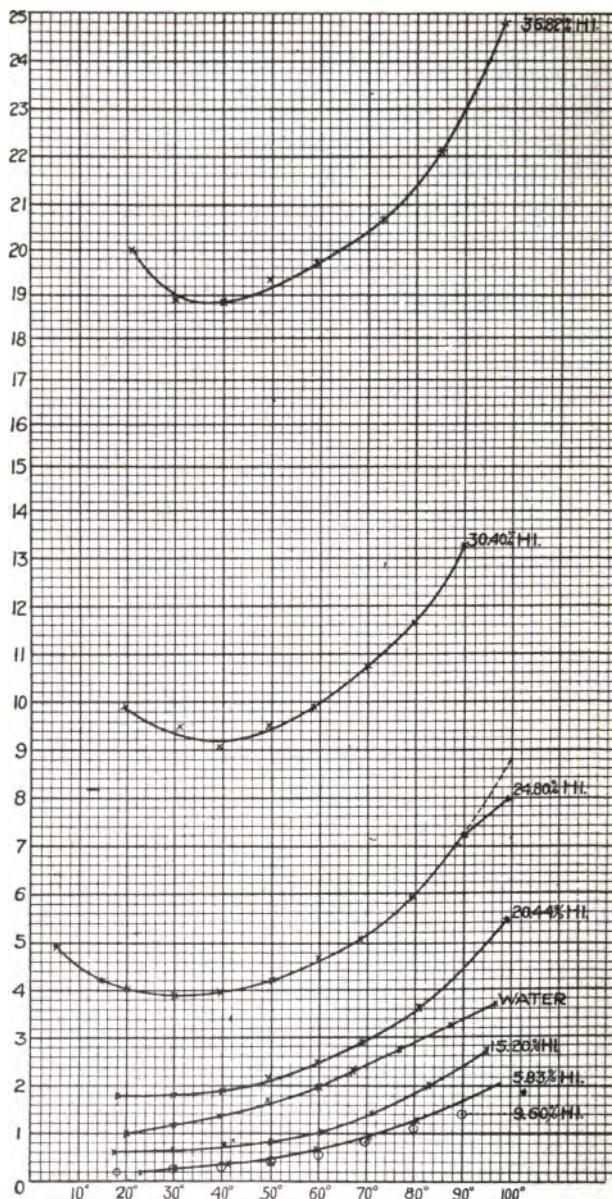
The second notable peculiarity in the result is that in concentrations of hydriodic acid, from twenty-five per cent. up, there is a very notable *increase* in the solubility with *decreasing* temperature from somewhere between  $30^{\circ}$  and  $40^{\circ}$ . This is most strikingly shown by the accompanying curves.

An inspection of these curves will readily show that there are distinct differences in their characters apart from the merely general increase or decrease in solubility occasioned by the different strengths of acid.

Comparing all curves for solubility in acid with that for solubility in water, it will be seen that the former all differ distinctly from the latter in two particulars. In the first place, above about  $40^{\circ}$  to  $50^{\circ}$  the solubility in acids increases more rapidly than does that in water, *i. e.*, the curves above this temperature are steeper for acids than for water. Below this temperature, however, the reverse is true, the curves being less steep for acids than for water, except that with acids of above twenty per cent. the pitch of the curve changes entirely between  $30^{\circ}$  and  $40^{\circ}$  and the solubility increases with decreasing temperature.

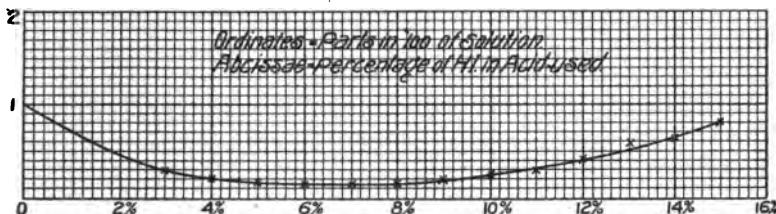
This abnormality would seem to indicate the introduction of a new system at lower temperatures, which, perhaps, becomes more and more stable with falling temperature, and by its greater solubility produces the peculiar character shown in the curves below  $40^{\circ}$ . The nature of this new system has been determined and will be made the subject of the following paper.

For convenience of reference the following table has been prepared. It contains the values for the solubilities of stannous iodide in water and hydriodic acid for temperatures from  $20^{\circ}$  to  $100^{\circ}$ . The values are taken from the points of intersection of the curves, and are expressed in parts per hundred of solvent instead of parts per hundred of solution as previously.



Curves showing solubility of stannous iodide at different temperatures in hydriodic acids of different strengths.

Ordinates = Parts stannous iodide in 100 of solution. Abscissae = Temperatures.



Curve showing solubility of stannous iodide in hydriodic acids of different strengths at 23.5° C.

TABLE II.

SHOWING THE VALUES FOR THE SOLUBILITY OF STANNOUS IODIDE IN VARIOUS CONCENTRATIONS OF HYDRIODIC ACID. VALUES TAKEN FROM INTERSECTIONS OF CURVES AND CALCULATED TO PARTS IN 100 OF SOLVENT.

| Per cent. strength of HI = | Water. | 5.83 | 9.60 | 15.20 | 20.44 | 24.80 | 30.40 | 36.82 |
|----------------------------|--------|------|------|-------|-------|-------|-------|-------|
| Temperature.               |        |      |      |       |       |       |       |       |
| 20°                        |        | 0.98 | 0.20 | 0.23  | 0.60  | 1.81  | 4.20  | 10.86 |
| 30°                        |        | 1.16 | 0.23 | 0.23  | 0.64  | 1.81  | 4.06  | 10.28 |
| 40°                        |        | 1.40 | 0.33 | 0.28  | 0.71  | 1.90  | 4.12  | 10.06 |
| 50°                        |        | 1.69 | 0.46 | 0.38  | 0.82  | 2.12  | 4.34  | 10.35 |
| 60°                        |        | 2.07 | 0.66 | 0.55  | 1.11  | 2.51  | 4.78  | 11.03 |
| 70°                        |        | 2.48 | 0.91 | 0.81  | 1.37  | 2.92  | 5.43  | 11.97 |
| 80°                        |        | 2.95 | 1.23 | 1.13  | 1.83  | 3.70  | 6.38  | 13.30 |
| 90°                        |        | 3.46 | 1.65 | 1.52  | 2.40  | 4.58  | 7.82  | 15.52 |
| 100°                       |        | 4.03 | 2.23 | 2.04  | 3.63  | 5.82  | 9.60  | ....  |
|                            |        |      |      |       |       |       |       | 34.05 |

STANFORD UNIVERSITY,  
July 17, 1897.

## ON IODOSTANNOUS ACID.

By S. W. YOUNG.

Received July 31, 1897.

A S has been pointed out in the previous paper, the solubility of stannous iodide in rather strong solutions of hydriodic acid, indicates the formation at low temperatures of a system of different character from that existing at higher temperatures.

In order to become more familiar with the facts of the case, the following experimental work was performed.

In the first place it was noticed that when saturated solutions of stannous iodide in hydriodic acid of about twenty-five per cent. or over, were cooled in ice-water, very light yellow needles crystallized out in greater or less quantity, and it was evident that these were entirely different in character from the red needles of stannous iodide itself.

Several unsuccessful attempts to dry samples of the product for analysis were made. In the first instance the product was filtered off by suction and transferred to a vacuum desiccator. It almost immediately began to turn red. A sample was next placed in a current of dry hydrogen, but this suffered the same discoloration as the first. It was next attempted to dry a sample in a current of dry hydrogen, the vessel containing the sample, as also the hydrogen, being kept at  $0^{\circ}\text{C}$ . by ice-water. Again the substance became red, but more slowly than in the previous experiments.

The most natural inference from these preliminary experiments was that the compound was iodostannous acid,  $\text{H}_2\text{SnI}_4$ , or  $\text{SnI}_2 \cdot 2\text{HI}$ , analogous to chlorostannous acid,  $\text{H}_2\text{SnCl}_4$ . It was thought that if this were the case it might be possible to dry the compound at low temperatures in an atmosphere of gaseous hydriodic acid. Accordingly a sample was placed in a weighing bottle, which in turn was placed in a wide-mouthed glass-stoppered bottle, which also contained pieces of glacial phosphoric acid. A current of dry hydriodic acid gas was then conducted into the bottle to displace the air, the bottle immediately stoppered tightly and immersed in ice-water. After a few hours, however, this sample too had begun to redden, and the attempt to obtain the composition of the body by direct analysis was abandoned.

In the meantime experiments were carried on to study more closely the solubility of the bodies at lower temperatures.

The method was to take hydriodic acid of known strength, add to it stannous iodide more than sufficient to saturate the solution, cool in ice-water and determine the amount of stannous iodide in the solution by titration with standard iodine solution by the process described in the previous paper. Following are the data obtained, all results being given in terms of stannous iodide:

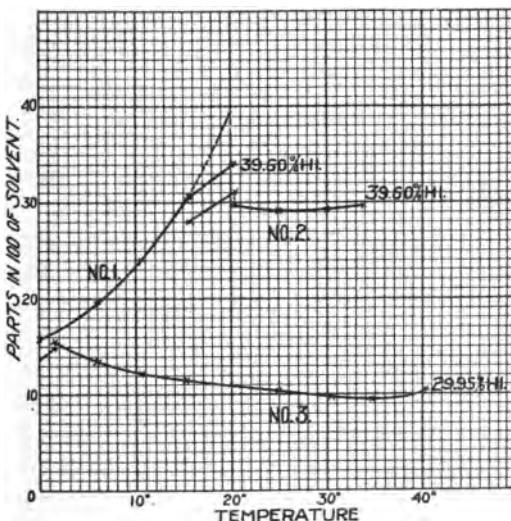
**SOLUBILITY OF STANNOUS IODIDE AT LOW TEMPERATURES IN 39.6 PER CENT. HYDRIODIC ACID.**

| Temperature.   | Parts in 100 of solution. |       | Parts in 100 of solvent. |
|----------------|---------------------------|-------|--------------------------|
|                | I.                        | II.   |                          |
| $0^{\circ}$    | 13.52                     | 13.56 | 15.66                    |
| $5.7^{\circ}$  | 16.44                     | 16.37 | 19.71                    |
| $10.5^{\circ}$ | 19.47                     | 19.60 | 24.27                    |
| $15.7^{\circ}$ | 23.56                     | 23.68 | 30.92                    |
| $20.3^{\circ}$ | 25.50                     | 25.60 | 34.30                    |

The solution gave out at this point and another one was prepared in the same way with the same acid. Readings in this case were begun at  $15.5^{\circ}$ .

| Temperature. | Parts in 100 of solution. |       | Parts in 100 of solvent. |
|--------------|---------------------------|-------|--------------------------|
|              | I.                        | II.   |                          |
| 15.5         | 22.00                     | 22.11 | 28.20                    |
| 20.2         | 23.49                     | 23.59 | 30.77                    |
| 20.1         | 22.93                     | 23.02 | 29.86                    |
| 25.3         | 21.98                     | ....  | 28.20                    |
| 30.0         | 21.97                     | ....  | 28.18                    |
| 34.7         | 22.49                     | ....  | 29.10                    |

After making the reading at  $20.2^{\circ}$  the solution was allowed to stand for some hours, at the end of which time the solid in the solution which at the time of the first reading had been of the light-yellow sort, had changed completely into red stannous iodide. The yellow compound was thus stable under the conditions of the experiment up to about  $20^{\circ}$ . By reference to the accompanying curves it will be seen that in the preceding set of



Curves showing the solubility of iodostannous acid and of stannous iodide at low temperatures. All parts soluble in terms of stannous iodide.

experiments also, the solubility diverges from the normal between  $15^{\circ}$  and  $20^{\circ}$ . It will also be noticed that in the present series of determinations the solubility falls from  $20^{\circ}$  to  $30^{\circ}$ , and

thereafter rises. This may perhaps be taken to indicate that the system represented by the yellow compound is more or less stable in solution after it has ceased to be stable in the solid form in contact with solution.

One other series of solubility determinations was made, using acid of 29.95 per cent. Following are the results of this series :

| Temperature. | Parts in 100 of solution. | Parts in 100 of solvent. |
|--------------|---------------------------|--------------------------|
| 1.5°         | 12.96                     | 14.89                    |
| 1.5°         | 13.15                     | 15.14                    |
| 6.0°         | 12.35                     | 14.09                    |
| 10.5°        | 11.01                     | 12.36                    |
| 15.2°        | 10.48                     | 11.70                    |
| 24.8°        | 9.36                      | 10.33                    |
| 30.7°        | 8.78                      | 9.62                     |
| 34.8°        | 8.70                      | 9.50                     |
| 40.3°        | 9.51                      | 10.50                    |

Between the two readings at 1.5° the same transition of the yellow solid into the red that was spoken of above as occurring at 20° had taken place. As is noticed it was not accompanied by any marked change in solubility as was the case above. It is also to be noticed that what change there is is toward increase, while in the previous case it was toward decrease. The probable explanation of this will be made later.

#### DETERMINATION OF THE COMPOSITION OF THE YELLOW COMPOUND.

It was shown above that the determination of the composition of the yellow compound by direct analysis appeared to be impossible. The composition of the body has, however, been determined by the following method :

If a solution of hydriodic acid of known strength be saturated, or nearly so, with stannous iodide at ordinary temperatures, and the amount of stannous iodide contained in the solution be then determined, it is evident that we may very easily calculate the amounts of stannous iodide and hydriodic acid contained in one hundred parts of water.

If now this same solution be cooled to, say zero, and the yellow compound be allowed to crystallize out, it is evidently possible by analyses of the mother-liquor to determine the percentages of hydriodic acid and stannous iodide remaining, and from

this to calculate the parts of stannous iodide and of hydriodic acid remaining in one hundred parts of water. Then, if the yellow body be a compound of stannous iodide with hydriodic acid, both the parts per hundred of water of stannous iodide and of hydriodic acid will be decreased, and the ratio of the decrease will be the same as the ratio in which the two constituents are combined in the yellow solid. Following are the data essential for the calculation.

1. Determination of the strength of the hydriodic acid, used by titration with standard alkali, gave :

| I.    | II.   |
|-------|-------|
| 35.91 | 35.96 |

2. After saturating the requisite amount of the above acid and filtering the solution through cotton-wool under oil, the percentage of stannous iodide was determined and found to be :

| I.    | II.   |
|-------|-------|
| 16.94 | 16.92 |

3. From these data it follows by simple calculation that the original solution was constituted as follows :

|                      |       |        |
|----------------------|-------|--------|
| Water .....          | 100   | parts. |
| Stannous iodide..... | 31.94 | "      |
| Hydriodic acid.....  | 56.14 | "      |

4. The solution was now cooled to  $0^{\circ}\text{C}$ . and allowed to stand for some time to insure equilibrium. Very considerable quantities of the yellow body separated out.

5. The percentage of stannous iodide was determined by the usual method and found to be :

| I.    | II.   | Average. |
|-------|-------|----------|
| 12.66 | 12.84 | 12.70    |

6. Since titrations with alkali cannot be made in presence of tin salts, the determination of the free hydriodic acid in the solution was found by taking weighed samples, diluting to 100 cc., and taking aliquot parts, and therein determining the total iodine by distilling off the iodine with ferric chloride in the Bunsen apparatus. Knowing the amount of stannous iodide in the solution already, the corresponding amount of iodine can be calculated. Subtracting this from the total iodine found, the remainder is the amount of iodine present as hydriodic acid. The follow-

ing determinations of total iodine in separately weighed samples were obtained :

| I.    | II.   |
|-------|-------|
| 38.73 | 38.55 |

Since the percentage of stannous iodide in this solution was found to be 12.70, it follows that the percentage of iodine in combination with tin is 8.71. Subtracting this from 38.60 (total iodine) gives 29.9 per cent. of iodine as hydriodic acid. This is equivalent to 30.14 per cent. hydriodic acid. Calculated to the basis of one hundred of water we get for the composition of the solution after crystallization :

|                       |       |        |
|-----------------------|-------|--------|
| Water .....           | 100   | parts. |
| Stannous iodide ..... | 22.22 | "      |
| Hydriodic acid .....  | 52.72 | "      |

These results show one hundred parts of water to have lost by crystallization 9.72 parts of stannous iodide and 3.42 parts of hydriodic acid, and these must be in combination in the yellow compound. A simple calculation shows this result to accord very closely with the formula  $\text{SnI}_2 \cdot \text{HI}$ , for

$$\begin{array}{ccccccc} \text{Mol. wt. } \text{SnI}_2 & : & \text{Mol. wt. HI} & : & : & \text{Amt. } \text{SnI}_2 & : x \\ 370.43 & : & 127.54 & : & : & 9.72 & : x \\ & & & & & x = 3.35. & \end{array}$$

Theoretically then, in the compound  $\text{HSnI}_2$ , or  $\text{SnI}_2 \cdot \text{HI}$ , the amount of hydriodic acid in combination with 9.72 parts of stannous iodide would be 3.35. The value found was 3.42, which, considering the complexity of the process, should be considered very fair agreement.

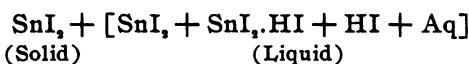
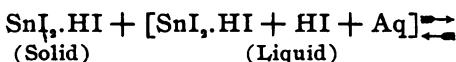
The fact that the compound contains only one molecule of hydriodic acid instead of two, as was at first thought possible, is not particularly surprising, since it appears to be generally true that those double halides of stannous chloride which contain only one molecule of the alkali chloride are the most stable.

#### EXPLANATION OF SOME OF THE PECULIARITIES NOTICED IN THE SOLUBILITY CURVES OF STANNOUS IODIDE AT LOW TEMPERATURES.

Certain peculiarities in the solubility curves accompanying are noticeable, and some of them have been pointed out. The sudden breaks in the curves are particularly noticeable. The fact that this

break is not seen in curve No. 1, is undoubtedly due to the fact that the observations were not carried far enough, the solution having given out at  $20^{\circ}$ . Breaks are noticed in curve No. 2, at  $20.2^{\circ}$ , and in curve No. 3, at  $1.5^{\circ}$ . Since these breaks indicate the points at which rapid decomposition of the iodostannous acid takes place according to the equation,  $\text{SnI}_2 \cdot \text{HI} = \text{SnI}_2 + \text{HI}$ , it follows that the iodostannous acid is stable at higher temperatures in contact with stronger acid. This is, of course, to be expected, since the stronger acid would exert greater pressure than would the weaker acid, against the entrance into the solution of new molecules of acid.

That decomposition of the solid iodostannous acid begins at temperatures lower than that at which it becomes wholly decomposed is shown by the falling off of curve No. 1 from the normal between  $15^{\circ}$  and  $20^{\circ}$ . That no definite temperature of transition exists between the two systems



is very evident, since the transformation of the first system into the second involves a great change in the nature of the solvent by increasing the concentration of the hydriodic acid and of the iodostannic acid, and by introducing a new factor, namely, stannous iodide. The transition is thus a gradual one, occurring over a considerable range of temperature. This is indicated by curve No. 1.

The falling solubility with increasing temperature from the point of complete change of the solid iodostannous acid into solid stannous iodide, must probably be taken to mean that even after the complete change has taken place in the solid forms, there remains in the solution more or less unchanged iodostannous acid. This becomes gradually transformed into stannous iodide and hydriodic acid, and the solution becomes supersaturated as to stannous iodide, which separates, causing the fall in solubility. This continues until all iodostannous acid is decomposed, or more probably, until further decomposition does not supersaturate the solution, and from that point the solubility increases

with the temperature. The curve does not, however, represent the true solubility of stannous iodide until all the iodostannous acid in the solution has been decomposed. This point may or may not agree with that at which the curve begins to rise.

Another peculiarity shown by the curves, which needs explanation, is the lack of coincidence between the portions of curves No. 1 and No. 2, which coincide as to temperatures. The experiments from which the two curves were obtained were made with the same solvent; namely, hydriodic acid of 39.60 per cent. It would seem at first sight that the portions of the two curves lying between 15° and 20° should coincide. The explanation of the lack of coincidence is, however, perfectly apparent. In making the solutions amounts of stannous iodide more than sufficient to saturate the solvent were used. The amounts were taken at random, so that in the two cases there were undoubtedly different excesses of stannous iodide. On cooling the solutions, iodostannous acid not only separates from the solution, but whatever excess of stannous iodide in the solid form may be present, provided it be not too great, is also converted into iodostannous acid. Thus the greater the excess of stannous iodide, the greater the demands made upon the solvent for hydriodic acid, and consequently the greater the weakening of the solvent as to hydriodic acid. Therefore, although both series of experiments were started with the same acid, the nature of the solvent will differ in the two cases after the cooling and the solubilities will naturally vary also.

It will be noticed that the break in the curve No. 2, at about 20° is caused by a sudden fall in solubility, while that in No. 3 at 1.5° is caused by a sudden rise in solubility. The explanation of this is entirely analogous to the foregoing. The direction of the change in solubility depends upon the relative solubilities of the two systems in whatever solvent may exist under the conditions.

As a matter of fact these sudden breaks are probably fictitious, and show in the curves only because sufficient time was not given at lower temperatures and at the temperatures of the breaks to attain perfect equilibrium, and also because the readings were not taken sufficiently close together.

The results of the work so far show mostly only qualitative

relationships. It is hoped soon to carry out a more exhaustive investigation upon the point, and also upon the similar chlorine and bromine compounds.

STANFORD UNIVERSITY,  
July 20, 1897.

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## A COMPARISON OF VARIOUS RAPID METHODS FOR DETERMINING CARBON DIOXIDE AND CARBON MONOXIDE.

By L. M. DENNIS AND C. G. EDGAR.

Received September 14, 1897.

THE value of gas analysis as an aid in the control and development of industrial processes is slowly being recognized by American manufacturers. Accompanying the increased use of this branch of analysis there seems to be, however, a tendency to adopt certain faulty methods of work to which it may be well to call attention. In industrial analyses chief stress will naturally be laid upon rapidity, and the accuracy demanded of the chemist will depend upon the nature of the work in hand. For example, in two processes in which carbon dioxide is regularly determined, it is sufficient in one case that the results be correct only within the range of one per cent., while in the other they should vary not more than one-tenth of one per cent. from the truth. In many cases, however, the analyst seems to be inclined to adopt some one form of apparatus and some one rapid method for the determination of each constituent and to adhere to this apparatus and method no matter what may be the conditions. Under such circumstances it is to be expected that the results obtained by different chemists on the same sample may show wide variations and even that the analyses of a single chemist, if his methods are not suited to the particular case in hand, may give rise to false deductions and cause financial loss to his employers. Difficulties similar to these were apparent, some years ago, in the analysis of iron and steel, and led to careful comparisons of the various methods by different chemists and to the development of standard methods of analysis. It was with the idea of making a beginning toward a similar comparison of some of the better known methods of gas analysis and of determining their relative accuracy and of ascertaining within what limits they might be relied upon, that Mr. Edgar undertook the

work described below. It is not claimed that the results show the absolute accuracy of the different methods, but they doubtless give quite closely their relative accuracy and the time which the average chemist would need for the various determinations.

The receiver for holding the gas mixtures to be analyzed consisted of a thick-walled, round-bottomed flask of about 700 cc. capacity. Into the neck of the flask was inserted a two-hole rubber stopper carrying two capillary glass tubes, one of these tubes ending just below the stopper and the other extending to the bottom of the flask. After firmly wiring the stopper, the flask was inverted and supported in a ring stand. The shorter capillary tube was connected by heavy rubber tubing with a level bottle containing about 800 cc. of mercury. The longer tube was bent in such a manner that it could easily be connected with the capillary of a Hempel gas burette. In collecting the samples for analysis, the air in the flask was first completely displaced by mercury from the level bottle and then measured portions of the gases to be mixed were run in through the longer capillary from a Hempel gas burette, this latter also containing mercury as the confining liquid. The flask was then shaken for five minutes and allowed to stand for some time, so that the gases might thoroughly mix. The gas mixture was at all times kept under a pressure slightly greater than that of the atmosphere, so as to prevent the possible entrance of air.

#### DETERMINATION OF CARBON DIOXIDE.

The gas mixture to be analyzed was prepared by mixing known volumes of air from outside the laboratory and carefully washed carbon dioxide prepared in a Kipp apparatus. The oxygen and nitrogen which might be contained in the carbon dioxide were not determined because the absolute accuracy of the different methods was in this work only of minor importance. Different mixtures of 500 cc. each were prepared, containing by measurement twenty, thirty, and forty per cent. of carbon dioxide. The solution of potassium hydroxide used for absorbing the carbon dioxide had the concentration recommended by Clemens Winkler;<sup>1</sup> namely, one part potassium hydroxide to four parts of water. The different forms of apparatus used were those devised by Honigmann, Bunte, Orsat, Elliot, and Hempel.

<sup>1</sup> Winkler: Lehrbuch der technischen Gasanalyse, 2te Auflage, 1892, p. 68.

Water was used in every case as the confining liquid. After each determination every measuring burette was rinsed with dilute hydrochloric acid to remove any potassium hydroxide that might accidentally have been introduced.

#### HONIGMANN'S BURETTE.

This was described to Professor Clemens Winkler by Moritz Honigmann, in a letter dated March 15, 1891. The method of using it which we adopted was that given by Winkler,<sup>1</sup> except that in filling the burette with the gas, instead of aspirating the gas through the burette until the air has been completely displaced, the burette was first filled with water which had been saturated with the gas, and the water was then displaced by gas from the receiver.

| Sample No. | Carbon dioxide. Per cent. | Check result with Hempel's apparatus. Per cent. | Results with Honigmann's apparatus. Per cent. | Time in minutes. |
|------------|---------------------------|---|---|------------------|
| I.         | 20                        | 19.9  | 19.6  | 10:00            |
|            |                           |   | 18.9  | 9:00             |
|            |                           |   | 19.1  | 9:30             |
| II.        | 20                        | 19.85   | 19.8  | 7:10             |
|            |                           |   | 19.8  | 6:30             |
|            |                           |   | 19.7  | 6:15             |
| III.       | 20                        | 20.1  | 20.0  | 6:00             |
|            |                           |   | 19.8  | 5:30             |
|            |                           |   | 19.8  | 5:00             |
| IV.        | 30                        | 29.9  | 29.2  | 6:30             |
|            |                           |   | 29.1  | 7:10             |
|            |                           |   | 29.0  | 5:40             |
| V.         | 30                        | 29.7  | 29.4  | 5:00             |
|            |                           |   | 29.5  | 5:00             |
|            |                           |   | 29.6  | 5:30             |
| VI.        | 30                        | 29.6  | 29.3  | 5:30             |
|            |                           |   | 29.4  | 5:15             |
|            |                           |   | 29.5  | 5:00             |
| VII.       | 40                        | 39.9  | 39.2  | 6:10             |
|            |                           |   | 39.0  | 6:00             |
|            |                           |   | 38.9  | 5:30             |
| VIII.      | 40                        | 40.1  | 39.7  | 6:00             |
|            |                           |   | 39.8  | 6:15             |
|            |                           |   | 39.2  | 5:35             |
| IX.        | 40                        | 39.9  | 38.9  | 5:30             |
|            |                           |   | 39.5  | 5:00             |
|            |                           |   | 39.4  | 6:10             |

<sup>1</sup> Winkler: Lehrbuch der technischen Gasanalyse, 2te Auflage, 1892, p. 82.

## AVERAGES WITH HONIGMANN'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20        | 19.6      |
| 30        | 29.2      |
| 40        | 39.31     |

BUNTE'S BURETTE.<sup>1</sup>

Method of use was as described by Winkler, p. 84.

| Sample No. | Carbon dioxide. Per cent. | Check result with Hempel's apparatus. Per cent. | Results with Bunte's apparatus. Per cent. | Time in minutes. |
|------------|---------------------------|---|---|------------------|
| X.         | 20                        | 19.9  | 19.8                                      | 8:30             |
|            |                           |   | 19.7                                      | 8:15             |
|            |                           |   | 19.8                                      | 8:35             |
| XI.        | 20                        | 20.1  | 19.8                                      | 8:30             |
|            |                           |   | 19.7                                      | 8:25             |
|            |                           |   | 20.1                                      | 8:50             |
| XII.       | 20                        | 20.0  | 19.8                                      | 8:10             |
|            |                           |   | 19.6                                      | ....             |
|            |                           |   | 19.8                                      | 8:00             |
| XIII.      | 30                        | 29.9  | 29.7                                      | 8:20             |
|            |                           |   | 29.8                                      | 8:45             |
|            |                           |   | 29.6                                      | 8:00             |
| XIV.       | 30                        | 30.1  | 29.9                                      | 8:20             |
|            |                           |   | 29.7                                      | 8:15             |
|            |                           |   | 30.0                                      | 8:40             |
| XV.        | 30                        | 29.8  | 29.8                                      | 8:10             |
|            |                           |   | 29.6                                      | 8:35             |
|            |                           |   | 29.7                                      | 8:15             |
| XVI.       | 40                        | 40.0  | 38.9                                      | 8:15             |
|            |                           |   | 39.3                                      | 8:00             |
|            |                           |   | 39.5                                      | 8:10             |
| XVII.      | 40                        | 39.8  | 39.5                                      | 8:25             |
|            |                           |   | 39.3                                      | 8:30             |
|            |                           |   | 39.5                                      | 8:00             |
| XVIII.     | 40                        | 39.9  | 39.3                                      | 8:00             |
|            |                           |   | 39.4                                      | 8:15             |
|            |                           |   | 39.5                                      | 8:25             |

## AVERAGES WITH BUNTE'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20        | 19.8      |
| 30        | 29.7      |
| 40        | 39.33     |

<sup>1</sup> *Journal für Gasbeleuchtung*, 1877, p. 447.

## ORSAT'S APPARATUS.

The form of this apparatus which we employed was that now made by Robert Muencke, Berlin, and it was used in the manner described by Winkler, p. 89.

| Sample No.    | Carbon dioxide.<br>Per cent. | Check result<br>with Hempel's<br>apparatus.<br>Per cent. | Results with<br>Orsat's<br>apparatus.<br>Per cent. | Time in<br>minutes. |
|---------------|------------------------------|--|--|---------------------|
| <b>XIX.</b>   | 20                           | 19.8   | 19.7   | 7:00                |
|               |                              |  | 19.6   | 8:00                |
|               |                              |  | 19.8   | 7:45                |
| <b>XX.</b>    | 20                           | 19.9   | 19.6   | 8:15                |
|               |                              |  | 19.7   | 8:00                |
|               |                              |  | 19.6   | 7:15                |
| <b>XXI.</b>   | 20                           | 19.8   | 19.5   | 8:10                |
|               |                              |  | 19.6   | 8:00                |
|               |                              |  | 19.5   | 7:50                |
| <b>XXII.</b>  | 30                           | 29.8   | 29.2   | 6:50                |
|               |                              |  | 29.3   | 7:00                |
|               |                              |  | 29.0   | 6:40                |
| <b>XXIII.</b> | 30                           | 29.7   | 29.2   | 7:00                |
|               |                              |  | 29.3   | 7:15                |
|               |                              |  | 29.3   | 8:00                |
| <b>XXIV.</b>  | 30                           | 29.9   | 29.3   | 7:00                |
|               |                              |  | 29.4   | 7:35                |
|               |                              |  | 29.3   | 7:40                |
| <b>XXV.</b>   | 40                           | 40.0   | 39.2   | 7:00                |
|               |                              |  | 39.1   | 6:10                |
|               |                              |  | 39.2   | 6:00                |
| <b>XXVI.</b>  | 40                           | 39.9   | 39.3   | 5:45                |
|               |                              |  | 39.2   | 6:00                |
|               |                              |  | 39.3   | 6:10                |
| <b>XXVII.</b> | 40                           | 39.8   | 39.4   | 6:50                |
|               |                              |  | 39.3   | 7:10                |
|               |                              |  | 39.4   | 7:00                |

## AVERAGES WITH ORSAT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20        | 19.62     |
| 30        | 29.45     |
| 40        | 39.46     |

## ELLIOT'S APPARATUS.

This apparatus is described in the *Chem. News*, 1881, 44, 289.

| Sample No. | Carbon dioxide.<br>Per cent. | Check result<br>with Hempel's<br>apparatus.<br>Per cent. | Results with<br>Elliot's<br>apparatus.<br>Per cent. | Time in<br>minutes. |
|------------|------------------------------|--|---|---------------------|
| XXVIII.    | 20                           | 19.8   | 19.7  | 6: 50               |
|            |                              |  | 19.6  | 7: 10               |
|            |                              |  | 19.7  | 7: 00               |
| XXIX.      | 20                           | 19.9   | 19.7  | ....                |
|            |                              |  | 19.6  | ....                |
|            |                              |  | 19.5  | ....                |
| XXX.       | 20                           | 20.0   | 19.8  | ....                |
|            |                              |  | 19.5  | ....                |
|            |                              |  | 19.8  | ....                |
| XXXI.      | 30                           | 30.0   | 29.6  | 8: 15               |
|            |                              |  | 29.5  | 8: 10               |
|            |                              |  | 29.6  | 8: 40               |
| XXXII..    | 30                           | 28.9   | 29.5  | ....                |
|            |                              |  | 29.7  | ....                |
|            |                              |  | 29.6  | ....                |
| XXXIII.    | 30                           | 29.9   | 29.4  | 7: 10               |
|            |                              |  | 29.6  | 7: 00               |
|            |                              |  | 29.5  | 6: 50               |
| XXXIV.     | 40                           | 39.9   | 39.2  | 6: 20               |
|            |                              |  | 39.3  | 6: 15               |
|            |                              |  | 39.0  | 6: 10               |
| XXXV.      | 40                           | 39.9   | 39.5  | 6: 50               |
|            |                              |  | 39.4  | 7: 00               |
|            |                              |  | 39.8  | 6: 35               |
| XXXVI.     | 40                           | 39.8   | 39.3  | 7: 00               |
|            |                              |  | 39.6  | 6: 50               |
|            |                              |  | 39.5  | 6: 10               |

## AVERAGES WITH ELLIOT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20        | 19.66     |
| 30        | 29.55     |
| 40        | 39.41     |

## HEMPEL'S APPARATUS.

The gas burette was that shown in Fig. 17 of the English edition of Hempel's Methods of Gas Analysis. The absorption pipette shown in Fig. 21, b, was employed, this being filled with iron wire gauze and potassium hydroxide, as described on page 157.

In some of the determinations given below the water was allowed to run down the walls of the burette for the usual time, three minutes. In others this time was shortened to one-half a minute to see whether the work could be hastened without too great a sacrifice of accuracy.

| Sample No. | Carbon dioxide.<br>Per cent. | Results with<br>Hempel's<br>apparatus.<br>Per cent. | Time allowed<br>for running<br>down of<br>water. | Time in<br>minutes. |
|------------|------------------------------|---|--|---------------------|
| I.         | 20                           | 19.9  | 3 min.   | 10:00               |
| II.        | 20                           | 19.85   | 3 "  | 9:00                |
| III.       | 20                           | 20.1  | 3 "  | 10:00               |
| X.         | 20                           | 19.9  | 3 "  | 8:50                |
| XI.        | 20                           | 20.1  | 3 "  | 9:00                |
| XII.       | 20                           | 20.0  | 3 "  | 8:40                |
| XIX.       | 20                           | 19.8  | 30 sec.  | 4:00                |
| XX.        | 20                           | 19.9  | 30 "   | 4:15                |
| XXI.       | 20                           | 19.8  | 30 "   | 4:09                |
| XXVIII.    | 20                           | 19.8  | 30 "   | 4:00                |
| XXIX.      | 20                           | 19.9  | 30 "   | 4:10                |
| XXX.       | 20                           | 20.0  | 30 "   | .....               |
| IV.        | 30                           | 29.9  | 3 min.   | 9:00                |
| V.         | 30                           | 29.7  | 3 "  | 9:00                |
| VI.        | 30                           | 29.6  | 3 "  | 9:00                |
| XIII.      | 30                           | 29.9  | 3 "  | 9:00                |
| XIV.       | 30                           | 29.9  | 3 "  | 9:50                |
| XV.        | 30                           | 30.1  | 3 "  | 9:00                |
| XXII.      | 30                           | 29.8  | 30 sec.  | 3:30                |
| XXIII.     | 30                           | 29.7  | 30 "   | 4:00                |
| XXIV.      | 30                           | 29.9  | 30 "   | 3:50                |
| XXXI.      | 30                           | 30.0  | 30 "   | 4:00                |
| XXXII.     | 30                           | 29.9  | 30 "   | 4:10                |
| XXXIII.    | 30                           | 29.9  | 30 "   | 4:05                |
| VII.       | 40                           | 39.9  | 3 min.   | 9:00                |
| VIII.      | 40                           | 40.1  | 3 "  | 8:45                |
| IX.        | 40                           | 39.9  | 3 "  | 9:00                |
| XVI.       | 40                           | 40.0  | 3 "  | 8:50                |
| XVII.      | 40                           | 39.8  | 3 "  | 9:00                |
| XVIII.     | 40                           | 39.9  | 3 "  | 9:00                |
| XXV.       | 40                           | 40.0  | 30 sec.  | 4:00                |
| XXVI.      | 40                           | 39.9  | 30 "   | 3:30                |
| XXVII.     | 40                           | 39.8  | 30 "   | 4:10                |
| XXXIV.     | 40                           | 39.9  | 30 "   | 4:15                |
| XXXV.      | 40                           | 39.9  | 30 "   | 4:25                |
| XXXVI.     | 40                           | 39.8  | 30 "   | 6:15                |

## AVERAGES WITH HEMPEL'S APPARATUS.

| Per cent. |                       | Per cent. |
|-----------|-----------------------|-----------|
| 20        | 3 min. running down   | 19.97     |
| 20        | 30 sec.      "      " | 19.87     |
| 30        | 3 min.      "      "  | 29.85     |
| 30        | 30 sec.      "      " | 29.87     |
| 40        | 3 min.      "      "  | 39.93     |
| 40        | 30 sec.      "      " | 39.89     |

## DETERMINATION OF CARBON MONOXIDE.

The gas mixture to be analyzed consisted of a mixture of nitrogen and carbon monoxide, the latter being prepared from oxalic acid. Mixtures containing by measurement three, nine, and fifteen per cent. of carbon monoxide were used. The gas was absorbed by means of a hydrochloric acid solution of cuprous chloride. For preparing this solution of cuprous chloride, we have used for some years in this laboratory the method which was suggested by Sandmeyer,<sup>1</sup> and which has been found superior to any other that we have tried.

The methods for determining carbon monoxide which were compared were those of Orsat, Elliot, and Hempel. After absorption by the cuprous chloride, the gas residue was always treated with potassium hydroxide, to free it from any acid vapors, before the final reading was made.

## ORSAT'S APPARATUS.

The gas sample was passed into the cuprous chloride tube and allowed to remain there for three minutes. It was then run back and forth from the burette for two minutes longer. Then it was passed into the potassium hydroxide tube and finally brought into the burette and measured.

<sup>1</sup> Sandmeyer: *Ber. d. chem. Ges.*, 17, 1633. Twenty-five parts of crystallized copper sulphate and twelve parts of dry sodium chloride are placed in fifty parts of water and heated until the copper sulphate dissolves. (Some sodium sulphate may separate out.) 100 parts of concentrated hydrochloric acid and thirteen parts of copper turnings are then added and the whole is boiled in a flask until decolorized. Platinum foil will hasten the process. The solution is kept in glass-stoppered bottles until wanted.

| Sample No. | Carbon monoxide.<br>Per cent. | Results with<br>Orsat's<br>apparatus.<br>Per cent. | Time in<br>minutes. |
|------------|-------------------------------|--|---------------------|
| I.         | 3                             | 2.3  | 13:00               |
|            |                               | 2.5  | 12:10               |
|            |                               | 2.2  | 11:00               |
|            |                               | 2.1  | 13:00               |
| II.        | 3                             | 2.0  | 12:10               |
|            |                               | 2.3  | 11:50               |
|            |                               | 2.7  | 12:30               |
|            |                               | 2.4  | 11:15               |
| III.       | 9                             | 8.4  | 14:00               |
|            |                               | 8.5  | 10:10               |
|            |                               | 8.4  | 10:30               |
|            |                               | 8.6  | 10:00               |
| IV.        | 9                             | 8.5  | 15:40               |
|            |                               | 8.4  | 11:00               |
|            |                               | 8.5  | 10:30               |
|            |                               | 8.7  | 10:45               |
| V.         | 15                            | 14.5   | 14:00               |
|            |                               | 14.2   | 15:00               |
|            |                               | 14.4   | 13:50               |
|            |                               | 14.6   | 14:10               |
| VI.        | 15                            | 14.7   | 16:10               |
|            |                               | 14.3   | 15:40               |
|            |                               | 14.6   | 14:00               |
|            |                               | 14.4   | 15:15               |

## AVERAGES WITH ORSAT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 3         | 2.31      |
| 9         | 8.5       |
| 15        | 14.4      |

## ELLIOT'S APPARATUS.

The gas was here also treated with potassium hydroxide after the absorption of the carbon monoxide.

| Sample No. | Carbon monoxide.<br>Per cent. | Results with<br>Elliot's apparatus.<br>Per cent. | Time in<br>minutes. |
|------------|-------------------------------|--|---------------------|
| VII.       | 3                             | 2.4  | 10:00               |
|            |                               | 2.3  | 10:30               |
|            |                               | 2.4  | 9:50                |
|            |                               | 2.1  | 10:10               |
| VIII.      | 3                             | 2.5  | 10:10               |
|            |                               | 2.3  | 11:00               |
|            |                               | 2.4  | 10:50               |
|            |                               | 2.0  | 10:30               |
| IX.        | 9                             | 8.4  | 11:00               |
|            |                               | 8.5  | 10:50               |
|            |                               | 8.3  | 11:40               |
|            |                               | 8.0  | 10:20               |
| X.         | 9                             | 8.4  | 13:00               |
|            |                               | 8.0  | 12:10               |
|            |                               | 7.9  | 11:50               |
|            |                               | 8.3  | 10:00               |
| XI.        | 15                            | 14.1   | 14:10               |
|            |                               | 13.9   | 15:00               |
|            |                               | 14.0   | 13:50               |
|            |                               | 14.4   | 14:30               |
| XII.       | 15                            | 14.0   | 14:00               |
|            |                               | 14.4   | 13:10               |
|            |                               | 13.8   | 13:40               |
|            |                               | 14.2   | 14:10               |

## AVERAGES WITH ELLIOTT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 3         | 2.3       |
| 9         | 8.2       |
| 15        | 14.1      |

## HEMPEL'S APPARATUS.

Two double gas pipettes were employed, the one which was used second containing a fresh solution of cuprous chloride.<sup>1</sup> The gas was passed into the first pipette, which was then shaken for two minutes; then into the second pipette and shaken for three minutes; then into a potassium hydroxide pipette, and finally into the burette, where it was measured.

<sup>1</sup> Hempel: Methods of Gas Analysis, p. 161.

| Sample No. | Carbon monoxide. Per cent. | Results with Hempel's apparatus. Per cent. | Time in minutes. |
|------------|----------------------------|--|------------------|
| XIII.      | 3                          | 3.2  | 10:10            |
|            |                            | 3.0  | 9:50             |
|            |                            | 2.9  | 10:00            |
|            |                            | 2.8  | 9:40             |
| XIV.       | 3                          | 2.8  | 10:00            |
|            |                            | 3.0  | 9:50             |
|            |                            | 2.9  | 9:30             |
|            |                            | 2.8  | 9:20             |
| XV.        | 9                          | 8.7  | 9:30             |
|            |                            | 8.8  | 9:10             |
|            |                            | 8.9  | 9:15             |
|            |                            | 8.8  | 9:30             |
| XVI.       | 9                          | 8.8  | 9:10             |
|            |                            | 9.0  | 8:50             |
|            |                            | 8.9  | 9:00             |
|            |                            | 8.7  | 8:45             |
| XVII.      | 15                         | 14.7                                       | 9:00             |
|            |                            | 14.6                                       | 8:40             |
|            |                            | 14.8                                       | 8:50             |
| XVIII.     | 15                         | 14.5                                       | 9:00             |
|            |                            | 14.7                                       | 8:30             |
|            |                            | 14.8                                       | 9:00             |

## AVERAGES WITH HEMPEL'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 3         | 2.9       |
| 9         | 8.85      |
| 15        | 14.77     |

The above results show that in the determination of carbon dioxide all of the five methods tested are accurate to within less than one per cent., and all except Honigmann's, to within one-half of one per cent., provided the amount of carbon dioxide present does not exceed thirty per cent. The most exact results in every case, however, are those obtained with Hempel's apparatus, and when the carbon dioxide is as high as forty per cent., this is the only method in which the error does not exceed five-tenths per cent. As regards speed, the Hempel method, with only thirty seconds allowed for the running down of the water, seems to have been the shortest, but was closely followed by the

Honigmann method. Attention may also be called to the fact that while in the methods of Honigmann, Orsat, and Hempel, the same potassium hydroxide is used repeatedly, in the Bunte and Elliot methods the reagent cannot be used twice, these methods being thus extremely wasteful.

In the determination of carbon monoxide the superiority of the Hempel method, both in accuracy and speed, is even more marked. Better results than those cited can be obtained with both the Orsat and Elliot apparatus but only by greatly prolonging the time.

CORNELL UNIVERSITY,  
JULY, 1897.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY  
No. 23.]

### THE ELECTROLYTIC DETERMINATION OF CADMIUM.

BY DANIEL L. WALLACE AND EDGAR F. SMITH.

Received September 9, 1897.

ABOUT a year ago Max Heidenreich<sup>1</sup> published an article in which he reviewed methods proposed by one of us (S) for the electrolytic determination of certain metals. In some instances he confirmed the observations of Smith, but in most cases differed with him. Recently S. Avery and Benton Dales<sup>2</sup> announced that so far as the determination of cadmium was concerned their "result was in complete harmony with the experiments of Heidenreich." In consequence of these experiences with the electrolytic methods suggested by Smith for the determination of cadmium, we have repeated them and offer new results obtained by us.

It was in 1878<sup>3</sup> that Smith stated that "0.1450 gram of cadmium oxide was dissolved in acetic acid, the excess of the latter expelled upon a water-bath and the platinum crucible then about half filled with water, and \* \* \* connected with the negative pole of a two-cell Bunsen battery \* \* \*. The deposition of the cadmium was regular \* \* \* a perfectly crystalline, grayish white layer." The precipitation was complete in about three hours. The experiment was repeated, but a bichromate battery was substituted for the Bunsen cells. At the time when these

<sup>1</sup> *Ber. d. chem. Ges.*, 29, 1585.

<sup>2</sup> This Journal, 19, 380.

<sup>3</sup> *Proc. Am. Phil. Soc.*, November, 1878.

trials were made, current strength in definite units was not given, hence subsequent workers have met with difficulty in repeating some of the early work, and perhaps that may account for the failure to precipitate cadmium from the solution of its acetate. We have sought to obtain the original working conditions given by Smith, have stated them in definite units, and append results obtained by their observance.

*Experiment 1.*—0.1329 gram of cadmium oxide was dissolved in acetic acid, the solution was evaporated to dryness, and the residue dissolved in thirty cc. of water. The liquid was then heated to 50° C., and electrolyzed with a current of 0.02 ampere for .thirty-seven sq. cm. of cathode surface. Voltage, 3.5. The metal was completely precipitated in four hours. It was crystalline and perfectly adherent. There was no evidence of sponginess. The hot, acid liquid was siphoned off and replaced by water without interrupting the current. We found that the period of precipitation could be diminished and very good results be obtained by adding one gram of ammonium acetate to the solution when the current had acted for an hour. The quantity of metallic cadmium present in this particular experiment was 0.1162 gram, while that actually found equaled 0.1158 gram.

*Experiment 2.*—0.1332 gram of oxide, treated precisely as outlined in Experiment 1, gave 0.1164 gram of adherent, crystalline metal instead of 0.1165 gram.

With these results before us we see no cause why the deposition of this metal from its acetate solution should be condemned. Neumann<sup>1</sup> mentions it as being possible, and Yver<sup>2</sup> even used an acetate solution in the electrolytic separation of cadmium from zinc.

Smith<sup>3</sup> published experiments made by him on the precipitation of cadmium from solutions containing free sulphuric acid. As this method seems not to have proved satisfactory in the hands of Heidenreich, and of Avery and Dales we have repeated the work and offer the following experiments as evidence in favor of the Smith method :

*Experiment 1.*—0.1270 gram of cadmium oxide was dissolved in two cc. sulphuric acid, sp. gr. 1.09, and the solution then

<sup>1</sup> Theorie und Praxis der analyt. Elektrolyse, p. 129.

<sup>2</sup> Bull. Soc. Chim., 34, 18.

<sup>3</sup> Am. Chem. J., 2, 41.

made up with water to thirty cc. It was heated to 50° C., and electrolyzed for a period of four and one-half hours with a current of 0.08 ampere for thirty-seven sq. cm. cathode surface. Voltage 2.5. The deposit weighed 0.1105 gram instead of 0.1111 gram. It was crystalline and adherent. Tendency to sponginess was not observed. The acid liquid was siphoned off before interrupting the current. The filtrate showed no signs of cadmium when tests were made for it.

*Experiment 2.*—In this trial 0.1358 gram of cadmium oxide was dissolved and treated as in Experiment 1. The deposit of metal weighed 0.1181 gram instead of 0.1188 gram.

We have never experienced any difficulty in the application of this method, and are also pleased to observe that Neumann<sup>1</sup> gives an example confirming the early recommendation of Smith. It is this: "die Lösung von 0.3 gram Kadmium sulfat in 150 cc. Wasser mit 1 bis 2 cc. verdünnter Schwefelsäure ver-setzt, wird auf 70 bis 80 Grad C., erwärmt und bei diesem Temperatur durch Ströme von 0.6 bis 1 Ampere zersetzt. Die Spannung schwankt ..... zwischen 2.5 bis 5 Volt ..... Der Niederschlag ist silberweiss."

Our experiences with the precipitation of cadmium from a phosphoric acid solution will be reserved for a subsequent communication.

We regard the double cyanide solution<sup>2</sup> as the best adapted for the deposition of cadmium. Further evidences of this are the many atomic weight determinations made of this metal, in which this particular solution was employed.<sup>3</sup>

The first suggestion for the electrolytic separation of copper from cadmium was also made by Smith.<sup>4</sup> He demonstrated that in the presence of free nitric acid copper was deposited in satisfactory form, while the cadmium continued in solution. Heidenreich,<sup>5</sup> in speaking of this method, which has received frequent confirmation, remarks: "eine Reihe von Versuchen, Kupfer von Kadmium aus einer freie Saltpetersäure enthaltenden Lösung zu trennen, führten zu keinem befriedigenden Ergeb-

<sup>1</sup> Loc. cit.

<sup>2</sup> Ber. d. chem. Ges., 25, 779.

<sup>3</sup> Ztschr. anorg. Chem., 1, 364; This Journal, 18, 1022.

<sup>4</sup> Am. Chem. J., 2, 43.

<sup>5</sup> Loc. cit.

nisse." In reply to this we offer the following experiments:

*Experiment 1.*—To a solution containing 0.3893 gram of copper sulphate (= 0.0988 gram of copper) and 0.1152 gram of cadmium oxide (= 0.0985 gram of cadmium) were added two cc. of nitric acid, sp. gr. 1.43. The total dilution of the solution equaled 100 cc. It was heated to 50° C., and electrolyzed with a current N.D.<sub>100</sub> = 0.10 ampere. Voltage 2.5. The metal was completely precipitated in three hours. It was bright in color and satisfactory in every respect. It weighed 0.0988 gram and did not contain cadmium.

*Experiment 2.*—A solution containing the same quantity of copper and 0.1203 gram of cadmium oxide, when treated exactly as in Experiment 1, gave 0.0987 gram of copper. It was free from cadmium.

To these results we would add the observation of Neumann:<sup>1</sup> "Am einfachsten ist zur trennung von Kupfer und Kadmium immer die Verbindung der mit *freier Saltpetersäure* versetzten Lösung beider Salze."

Heidenreich maintains that the separation of copper from cadmium succeeds "sicherer aus einer mit *Schwefelsäure* versetzten Lösung."<sup>2</sup> This solution had been previously recommended by Smith,<sup>3</sup> and his observations were confirmed by Freudenberg.<sup>4</sup>

The results recorded in the preceding paragraphs justify us in saying that cadmium can be successfully determined electrolytically when working either with its acetate or sulphate, and that its separation from copper in the presence of nitric acid is in every respect satisfactory.

The failure of Heidenreich to precipitate uranic oxide by means of the current will be considered later.

UNIVERSITY OF PENNSYLVANIA.

## ON THE REACTIONS BETWEEN MERCURY AND CONCENTRATED SULPHURIC ACID.

BY CHARLES BASKERVILLE AND F. W. MILLER.

Received September 16, 1897.

MANY text-books class the reactions between copper and concentrated sulphuric acid along with mercury and sul-

<sup>1</sup> *Elektrolyse*, p. 169.

<sup>2</sup> See *Electrochemical Analysis*, 2nd. Ed., p. 108.

<sup>3</sup> *Ztschr. phys. Chem.*, 12, 97.

phuric acid, stating merely that a sulphate of copper or mercury is formed with the evolution of sulphur dioxide.

In other communications<sup>1</sup> one of us, (Baskerville) has shown that while the formula

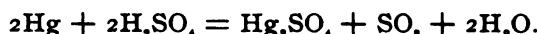


expresses in fact the main reaction when these two substances are brought together, even at different temperatures, that only at 270° C., or higher, is that reaction unaccompanied with very important and complex secondary reactions. In preparing sulphur dioxide, by heating together copper and concentrated sulphuric acid, invariably a black or brown material discolors the colorless acid. This dark substance is, in the main, cuprous sulphide.

Not finding the reaction between mercury and concentrated sulphuric acid worked out in detail in any of the literature at our command and since so much wrong data have been recorded concerning copper under similar conditions, it was deemed advisable to study this reaction at different temperatures.

The reaction is by no means like that of copper. The primary reaction depends upon the preponderance of mercury or acid, the temperature, and the time during which it is allowed to continue.

If the mercury be in larger amounts than the acid, invariably almost pure mercurous sulphate is produced :



It will be well to state here that the mercurous sulphate so produced is a white crystalline substance and not black, as stated in Roscoe and Schorlemmer's Treatise on Chemistry.<sup>2</sup>

Series of experiments in duplicate were carried out at different temperatures when the acid was in large excess. A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C. This experience is contrary to that stated in a number of text-books. Experiments carried out at 100° C. upon a water-bath, lasting during twenty hours, in apparatus especially arranged to insure only the presence of dust-free, dry air

<sup>1</sup> This Journal, 17, 904, and 18, 942.

<sup>2</sup> Vol. II. Part I. p. 401.

showed that about one-fifth of the mercury had entered into the reaction. Ten grams of the mercury and from fifty to 100 grams acid were used. Expecting the results to exhibit this reaction,



we were surprised to find so much less sulphur dioxide evolved than should have been. The crystalline sulphate produced gave 20.75 per cent.  $\text{SO}_2$ , which is very near 19.35 calculated for mercurous sulphate. Again, at 150° C., when the flask containing the mercury and acid was kept at a practically constant temperature by being immersed in a sulphuric acid bath for two hours, the amount of sulphur dioxide evolved was much below the theoretical. At least half of the mercury in each of these experiments was dissolved. The white crystalline layer of sulphate which separated out as the amount of metallic mercury decreased was augmented by another layer, which had been in solution, when the acid became cool. Both were crystalline, but while the latter was powdery the former was composed of needle-like crystals. To avoid the formation of the basic sulphate,  $\text{HgSO}_4 \cdot 2\text{HgO}$ , which was always produced in our efforts to wash out the remaining acid with water, we used ninety-five per cent. alcohol. Four washings were sufficient; in fact, on further washing even with alcohol some basic sulphate was formed. On analysis of this alcohol-washed substance, which had been dried to a constant weight at 100° C., we obtained:

|                     | Calculated for<br>$\text{Hg}_2(\text{SO}_4)_2$ , or $\text{Hg}_2\text{SO}_4 \cdot \text{HgSO}_4$ . | Found. |
|---------------------|--|--------|
| $\text{SO}_4$ ..... | 24.24  | 23.96  |
| Mercury (-ous)..... | 50.38  | 24.27  |

At 200° C. the percentage of mercurous mercury dropped to 40; at 250° C. still lower, showing a steady decrease in the amount of mercurous sulphate produced as the temperature increased. When the acid was boiled and the mercury poured in, the crystalline compound gave 32.91 per cent. of sulphur tetroxide when mercuric sulphate contains 32.43 per cent. Evidently some of the acid was not removed by the washing with alcohol.

It was desirable to determine whether the primary reaction took place in steps, *e. g.*, if the metal liberated hydrogen, which

in the nascent state attacked the remaining sulphuric acid with the production of sulphur dioxide, such having been recorded by some authors to be the case in the reaction between copper and sulphuric acid. Careful experiments at different temperatures, 150° and 200° C., were carried out in an atmosphere of carbon dioxide free from air. One hundred cc. of the gases given off and collected over a ten per cent. solution of sodium hydroxide gave not a trace of hydrogen. The sulphuric acid in this case is evidently reduced directly by the metal. No sulphide was produced, nor any free sulphur.

If portions of the crystalline compound, produced by the treatment of mercury with concentrated sulphuric acid rendered free of acid by washing with alcohol and dried at 100° C., be again treated with acid in similar apparatus, sulphur dioxide is evolved in proportion to the amount of mercurous sulphate there is present. If mercuric sulphate be treated with the acid no sulphur dioxide is evolved. In fact, if a prepared mixture of mercurous and mercuric sulphates in varying proportions, or any of the crystalline compounds obtained in any of the experiments cited, except that produced by the boiling acid, be treated with fresh acid and heated until the gas evolved ceases to bleach a weak potassium permanganate solution, the crystalline residue then obtained is mercuric sulphate.

Although the relative yield of sulphur dioxide is less, the treatment of mercury with concentrated sulphuric acid has been recommended for classroom experiment on account of neatness and freedom from black residue, which in the case of copper is oftentimes unintelligible to the ordinary student. A slight objection may be urged against this use on account of the volatility of the metallic mercury at the temperature of reaction. Faraday has shown that in spite of its high boiling-point, mercury volatilizes at the ordinary temperatures. One of us (Baskerville) has had this fact to contend with in several cases where this method of evolving sulphur dioxide was made use of in quantitative work.

In the experiments given all materials used were pure. The concentrated sulphuric acid was of 1.84 sp. gr. The mercury was purified according to Lothar Meyer's method<sup>1</sup> by allowing

<sup>1</sup> *Ztschr. anal. Chem.*, 2, 241.

the distilled metal to flow in a thin stream first through a column of dilute nitric acid, then dilute sulphuric, to dissolve out all lead and tin, finally washed and dried. All apparatus was most carefully cleansed, and when necessary moisture-free and proved to be air-tight.

UNIVERSITY OF NORTH CAROLINA,  
July, 1897.

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## ON THE DETERMINATION OF FAT AND CASEIN IN FECES.

BY HERMAN POOLE.

Received August 24, 1897.

HAVING been called upon to make some examinations of feces from children in connection with the clinical experiments on the Prof. Gaertner mother-milk now being carried on with satisfactory results at the German Polyclinic on Seventh Street, New York City, I began by looking up what had been done on the subject previously. To my surprise I found nothing at all which would give even a fairly approximate idea of the percentage of fat and casein. After consulting all the authorities I could find, I saw that I must work out a new or a fuller method than any previously used.

The problem to solve was this: A certain child takes per day a definite quantity of milk of known composition. It digests a portion of this and passes off the balance undigested. This milk contains fat and casein. How much fat and how much casein pass through undigested, and from this how much of the milk is assimilated?

Of course, one of the first books suggested to an American would be Flint's Physiology, since Flint has done considerable work on this kind of material several years ago. An examination of his work, however, showed that the methods he used and the special objects he had in view were entirely unsuited and foreign to the work I intended. He operated on the feces of adults, and more particularly to discover and extract the unknown and undescribed constituents rather than to actually make accurate determinations of the common and known ones. Besides, the chemical methods in use in his day are to a considerable extent supplanted by more accurate and modern methods.

Papers have been published and articles written on the analyses of feces for certain purposes by Rubner, Camerer, Prausnitz, Mayer, and Constanidini in the *Zeitschrift für Biologie* in most of the volumes since 1879, and by Malfatti and Strumpell,<sup>1</sup> but none of these in any way outline methods which would be used in my investigation. The fullest account given is that by Prausnitz,<sup>2</sup> in which he sums up what has been done and gives the result of the most recent work up to that time.

But all these methods are insufficient, not carrying the analysis far enough. Neither attempts to separate the fat or the casein in a state approaching freedom from other allied or commixed substances. All give the results of imperfect separations.

The fat determinations are all made by drying the material at 100° and then extracting with ether. This ether extract is evaporated; the residue is weighed and calculated as fat. This would be a very simple and easy method, but, unfortunately, it is not correct and can give only misleading deductions. In addition to the fatty matter, ether dissolves cholesterol and some of the bile and other products. The proportion of cholesterol is not constant, varying from twenty-five to seventy-five per cent.; the amount contained varies from day to day with the same child, and even varies with the successive passages. Still greater then must be the variation with different children. The proportion of the other substances is small and may be neglected ordinarily. It will be easily seen, therefore, that deductions based on such determinations must be faulty.

In the determination of casein no satisfactory method has yet been devised that I know of. The authorities cited have taken the ether extract, the water extract, and the alcohol extract; the residue was then treated by some method for determining the nitrogen and it was given as such, no attempt being made to separate the nitrogen of the food, digested or undigested, from that of extraneous bodies which might be present. This method is even more faulty than the fat determination. It shows the amount of nitrogen passing off through this channel but gives no idea as to the form in which it occurs.

<sup>1</sup> Konig's *Chem. der Mensch. Nahrung und Genuss*, I, 37 and 46.

<sup>2</sup> *Ztschr. für Biol.*, 1894, pp. 328 et seq.

The insoluble residue, after the three menstrua above mentioned have been used, contains the insoluble casein, the insoluble fatty acid compounds (usually lime, alumina, and iron as bases) and the broken down epithelium cells gathered from the whole length of the intestinal tract. This waste epithelium is at times quite an important factor and is always present in an appreciable degree as can be seen by a microscopic examination. The fatty acid compounds, of course, contain no nitrogen. The three menstrua fortunately remove most of the numerous nitrogenous substances present in the original material, leaving only a small quantity not in the epithelium cells or in the casein; so that it may be considered that the remaining undissolved mass consists substantially of the last two.

The problem then becomes one of separating the cholesterol from the fat and the casein from the epithelium cells and other foreign matter.

First, separation of the fat and cholesterol. The ether extract containing these two and the coloring matter from the bile is sometimes yellow, sometimes brown or greenish. It always contains some substances insoluble, or difficultly soluble, in alcoholic potash, which is used for saponification and solution of the fat and cholesterol.

The ether extract is evaporated nearly dry at 100° C. and then heated at 110° C. till dry. This heating to 100° is necessary, since, although ether is used as a solvent, this ether always contains a little water, sometimes more than will be driven off at 100°. The residue is then saponified with alcoholic potash, which usually leaves only a small portion undissolved. When thoroughly saponified, water is added and the whole boiled to expel the alcohol. Then more water is added, if needed, and the solution filtered. The filtrate should be clear and opalescent, but is usually colored. Now pour the filtrate into a separatory globe or cylinder and agitate thoroughly with an equal bulk of ether. Allow to stand and separate. Draw off the liquids separately and again treat the heavier one with ether as before. A further treatment with ether usually reveals only slight traces of cholesterol and need not be made. The liquid thus freed from cholesterol is now evaporated nearly dry and dissolved in water. It contains the fat acids, which may be determined by any of the usual

methods, and multiplication by the proper factor will give the amount of butter fat originally contained in the feces as such.

Secondly, the separation of the casein from the other substances. This is a difficult separation. None of the strong solvents, alkalies, strong acids, etc., can be used as they destroy both, or while attacking one, attack the other. Neutral salts are not satisfactory for dissolving insoluble casein since large quantities of liquid must be used, and even then a second treatment with the same solvent will usually dissolve more.

The method which I finally adopted, while not entirely satisfactory, still gives results far nearer the truth than any of the published ones and, at least for the purpose in view, comparable results.

The feces are extracted in succession by ether, water, and alcohol, and then dried. The residue is digested for several hours (usually over night) in a mixture of thirty parts hydrochloric acid and seventy parts water at a temperature of about 50° C. This dissolves the casein and leaves the epithelium débris and other substances. The fatty acid compounds are of course decomposed, but do not influence the result at all. Hydrochloric acid is more satisfactory than the neutral salts and gives fairly concordant results on duplicate trials. After cooling sufficiently, the liquid is filtered off, evaporated, and the nitrogen determined by the Kjeldahl method. From this the quantity of casein is calculated and the percentage determined.

In a careful, thorough analysis the quantity of fatty acids in the insoluble soap would of course be determined, but with my investigation this is not necessary, as they usually represent digested or partially changed fats, and I am looking only for the undigested portions.

My results of course are much lower than would be obtained by the old method, but I claim they are nearer the truth and perfectly comparable among themselves. They certainly do show more nearly the composition of the material examined and furnish a better guide as to the workings of the food on the child and the child on the food.

No percentage results are given in this paper as no work has yet been done on perfectly healthy children, and such work is needed as control.

The investigation will be pursued and if possible more satisfactory methods devised. Any suggestions from chemists having experience in this line will be thankfully received.

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### THE PRINCIPAL AMID OF SUGAR-CANE.

By EDMUND C. SHOREY.

Received October 4, 1897.

IT has been more than forty years since Lawes and Gilbert pointed out that in plants used as feed for stock, part of the nitrogen exists in the amid form. Since then several schemes of analysis have been devised by which to determine the amounts of different forms of nitrogen in plants, and numbers of analyses have been published in accordance with these schemes, so that it has come to be generally accepted by chemists that a part of the nitrogen of all plants, in the growing stage at least, is in the amid form. E. Schulze, who has done more than anyone else to advance our knowledge of the forms in which nitrogen exists in plants, states that the amid compounds vary with different plants, and also with the age and condition of the plant.

In 1892 I determined the total and albuminoid nitrogen content of a number of samples of mature sugar-cane. In the samples then examined I found the albuminoid to be about ninety per cent. of the total nitrogen. Analyses made later of another and less mature variety of cane, showed this non-albuminoid nitrogen to be sometimes as high as twenty-five per cent. of the total nitrogen. The albuminoid nitrogen was determined by precipitating with cupric hydroxide, taking special precautions to prevent any decomposition of the albuminoids by preliminary heating. No attempt was made at that time to determine the character of the non-albuminoid nitrogen.

In January, 1894, a paper was read by W. Maxwell before the Louisiana Sugar Planter's Association on "Organic Solids not Sugar in Cane Juice." The matter of this paper was subsequently issued as a bulletin by the Louisiana Experiment Station. In this paper attention was drawn to the fact already noticed, that all plants contain at some period part of their nitrogen in the amid form: a fact well known to chemists, but apparently overlooked by sugar manufacturers. After giving a number of analyses of cane juice, in which the difference

between the total and albuminoid nitrogen was designated amids, Maxwell stated that the amid of cane juice was found to be asparagin, crystallized preparations of this body having been obtained. He made, however, no statements regarding the physical or chemical properties of the asparagin obtained, nor did he give any information as to how it was ascertained to be asparagin.

Some months after the publication of this paper, there was a discussion in the *Bulletin de l'Association des Chimistes de Sucrerie* between H. Pellet and W. Maxwell as to the possibility of the asparagin of cane juice affecting the polaroscopic reading of such solutions. In view of this possibility I determined to make some preparations of the amid compound or compounds in cane juice, and ascertain the rotatory power of the same. This work was begun in January and continued until July of the present year, and covers every variation in age and condition of cane delivered at the mill this year, as well as some samples of very young cane.

As a result of this work I have found that the principal amid compound present in sugar cane is *not optically active*, and is *not asparagin*, but glycocoll or glycocin, an amid not heretofore known to occur in plants.

The method of separating the amid was that commonly used, *viz.*, precipitation with mercuric nitrate. To the juice obtained from the cane sample by pressure, a slight excess of lead subacetate was added, the liquid filtered, and to the filtrate an acid solution of mercuric nitrate was added, and the whole brought to faint acidity if strongly acid, by the cautious addition of caustic soda. The precipitate thrown down, which was white and flocculent, after being well washed, was decomposed by hydrogen sulphide. The filtrate from the mercuric sulphide, after being concentrated to a thin syrup, was allowed to stand, when abundant, well defined crystals were generally formed in thirty-six hours. The filtrate from the mercuric sulphide was always quite strongly acid, and the subsequent crystallization was found to be much more rapid, and the yield larger if the solution were neutralized with ammonia before concentration, and neutrality maintained during concentration by the continued addition of ammonia as the solution became acid again.

This addition of ammonia made no difference in the character of the crystalline body obtained. The crystals after separation from the mother-liquor were purified by recrystallizing twice.

The mercuric nitrate used was prepared as wanted by boiling mercury with an excess of nitric acid until no further reaction for mercurous nitrate was obtained. I have as yet made no analysis of the white insoluble precipitate which mercuric nitrate gives with the amid body in question.

The purified crystals were in the form of plates or four-sided prisms, belonging to the monoclinic system; glassy in appearance, quite hard, grating between the teeth and having a sweetish taste. They were soluble in cold water, but much more readily in hot, soluble in eighty per cent. alcohol, but insoluble in ether. In all, fifteen preparations of these crystals have been obtained, and in all cases the physical properties of the crystals and the chemical properties of the solution have been the same.

The mother-liquor from the crystals was found to contain other nitrogenous bodies not readily obtained in a crystalline form, the nature of which has not yet been ascertained; but they are comparatively small in amount, and, since nearly the whole of the bodies precipitated from cane juice by mercuric nitrate can be obtained in a single crystalline form having the properties of an amid, it is quite justifiable to speak of this body as the principal amid of sugar-cane.

In examining this sugar-cane amid to ascertain if it were optically active, solutions containing from two to four grams of the substance per 100 cc. of water were examined in a 200 mm. tube of a Schmidt and Haensch half-shade polariscope, observations being also made on similar solutions after the addition of caustic soda or nitric acid. In no case was any rotatory power shown. As asparagin is slightly left-handed in water-solution, more strongly so in alkaline solution and strongly right-handed in acid solution it was at once evident that the sugar-cane amid must be an inactive form of asparagin, or some other body not asparagin. A more extended examination soon brought out other points of difference between the sugar-cane amid and asparagin; and on comparison of the properties of this amid with those of the other known bodies, it was shown unmistakably to be glycocoll.

The chief points of difference between asparagin and the sugar-cane amid may be stated as below :

|  | Sugar-cane amid.   | Asparagin.   |
|--|--|--|
| Optical activity.                          | Inactive.  | Left-handed in water solution.                                 |
| Water of crystallization.                  | None.  | One molecule lost at 100° C.                                   |
| Behavior with Fehling's solution.          | Does not reduce on boiling.  | Reduces on boiling.  |
| Behavior when boiled in alkaline solution. | Gives off NH <sub>3</sub> only if alkali is quite concentrated, leaving HCN in solution. | Gives off NH <sub>3</sub> , leaving aspartic acid in solution. |

It will be noted that these properties of the sugar-cane amid are identical with those of glycocoll, and in addition to this correspondence, both produce a gray precipitate of metallic mercury when added to a solution of mercurous nitrate, and both give a red coloration with ferric chloride.

The reaction by which the sugar-cane amid is most readily distinguished from asparagin, and by which also its identity with glycocoll is thoroughly established, is that which results on heating in alkaline solution. As is well known, asparagin gives off ammonia when heated in quite dilute alkaline solution, leaving aspartic acid in solution. On the other hand, glycocoll and the sugar-cane amid do not give off ammonia when heated in alkaline solution unless such solution be strongly alkaline, and after the evolution of ammonia has ceased no aspartic acid is found in the solution, but if hydrochloric acid be added to acidify and the solution heated, hydrocyanic acid is given off and can be detected by the smell, and oxalic acid is left in solution and can be precipitated as calcium oxalate. When operating with very small quantities of the amid, as I often found it necessary to do, the quantity of hydrocyanic acid given off in this reaction is so small that the smell is masked by that of the hydrochloric acid; in this case the presence of hydrocyanic acid can be established in the usual way by placing a drop of yellow ammonium sulphide on a porcelain dish, holding over the boiling solution for a few seconds, removing the excess of sulphide by blowing, and prov-

ing the presence of a thiocyanate by the red coloration produced on addition of ferric chloride.

The sugar-cane amid also gives off hydrocyanic acid when heated with dilute sulphuric acid and manganese dioxide.

When heated in a sealed tube with benzoic acid, the sugar cane amid gives hippuric acid, a condensation characteristic of glycocoll, and one by which it is supposed hippuric acid is formed in the animal body.

The hippuric acid so formed was identified by separating it from any remaining benzoic acid by agitation with petroleum ether evaporating the insoluble residue to dryness with nitric acid and heating, when the characteristic smell of nitrobenzol was detected.

Glycocoll has been prepared in the usual way from hippuric acid by boiling with dilute sulphuric acid, and the reactions given above as characteristic of that body have been verified throughout.

It having been thus thoroughly established that the principal amid of sugar-cane is glycocoll, it is well to note that there are certain points in which glycocoll resembles asparagin, and the resemblance is such that anyone prone to jump at conclusions would on obtaining a crystallized preparation of the sugar-cane amid immediately pronounce it asparagin. The points of resemblance are these: first, the general appearance, solubility, etc., of the crystals; second, neither gives up any nitrogen when treated with sodium hypobromite in alkaline solution; third, both dissolve cupric hydroxide to a blue solution; and fourth, both contain the same per cent. of nitrogen. Asparagin crystallized with one molecule of water of crystallization and glycocoll each contain theoretically 18.66 per cent. nitrogen, while the average of all samples of the sugar-cane amid was 18.69 per cent. The Gunning method was used in determining the nitrogen, and clean, well-defined crystals were selected for such determinations.

In all, fifteen preparations of the glycocoll have been made from sugar-cane; and the samples of cane from which it has been prepared have included young shoots of cane a few weeks old, the green tops of cane one year old, and mature cane growing at elevations from 400 to 1,200 feet above sea-level. It is fair then

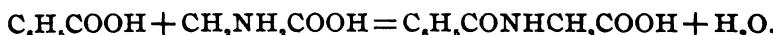
to conclude that glycocoll is not only the principal amid of sugar-cane, but is also a normal constituent of this plant at all periods of its growth.

I have as yet made no attempts to estimate the quantity of glycocoll in sugar-cane or any of its products, but have noticed that larger amounts have been obtained from young than from mature cane.

The average nitrogen content from mature sugar cane is probably about 0.30 per cent., and of this at least 0.22 per cent. is albuminoid nitrogen; so that the amido content cannot be higher than 0.08 per cent., and probably is often less than 0.02 per cent. It is easily seen then that the preparation of any quantity of the sugar-cane amid entails considerable labor, and this coupled with the fact that this work has been done at odd times during a busy grinding season, is my excuse for the incompleteness of this research in some respects.

The identification of glycoçoll, glycocene, or amido acetic acid in sugar-cane is of interest from several points of view. Its occurrence has not been noted in a plant before, and it has been considered a body belonging wholly to animal chemistry. It can be prepared from gelatin by heating with acids or alkalies, in fact, was first prepared in this way, and it has been supposed that it was formed in the animal body from gelatin or gelatin-yielding proteids.

It does not seem to occur free in the animal body, and the theory of its formation from proteids seems to have been demanded by the following fact : Benzoic acid, when taken into the stomach, appears in the urine as hippuric acid, and to explain this it has been supposed that the condensation already referred to takes place; *viz.*, benzoic acid and amido acetic acid combine to form hippuric acid with the elimination of water.



This view is strengthened by the fact that when glycocoll is taken with benzoic acid the yield of hippuric acid is increased.

In the urine of herbivorous animals hippuric acid occurs in relatively large quantities, and while the food of such animals has been deemed capable of supplying the benzoic acid part, the

source of the glycocoll to form such large quantities of hippuric acid has been more or less of a puzzle to physiologists.

The identification of glycocoll in sugar-cane and the fact that it has been mistaken for asparagin suggests the probability of its occurrence in other plants, especially the *Graminae*, which form the major part of the food of herbivorous animals; and it is quite likely that the source of the hippuric acid in the urine of such animals will be found in such occurrence.

In vegetable, as in animal physiology, the question of the constitution of proteids is uppermost. Now glycocoll in the physiology of sugar-cane no doubt plays the same part which other amids are known to do in other plants. It is the form in which nitrogen is conveyed to growing parts, and when maturity is reached the amid becomes the albuminoid to become the amid again when a new growth takes place. A number of facts collected during this study of the sugar-cane amid point to the existence in cane of a gelatin or gelatin-yielding proteid which yields glycocoll as one of the products of decomposition. This coupled with the well known and comparatively simple constitution of glycocoll seems a step toward the understanding of at least one proteid of sugar-cane. The further study of this matter promises to be of special interest, both from a physiological and a technical point of view.

From the sugar manufacturer's point of view the presence of glycocoll presents the following points of interest: It is known that at various stages of sugar manufacture ammonia is given off from boiling cane juice, especially if this juice has been rendered alkaline by an excess of lime. This has been stated as due to the decomposition of asparagin into aspartic acid and ammonia. But since we know that the amid is glycocoll and not asparagin, and that glycocoll is not decomposed unless boiled in strongly alkaline solution, it is plain that the ammonia must be derived from the decomposition of albuminoids. When, as is generally the case, cane juice is maintained approximately neutral throughout the course of manufacture, the whole of the glycocoll originally present in the juice should be found in the final molasses.

Whether this theory always carries out in practice, I have not yet ascertained, but I have obtained glycocoll in comparatively

large quantities from several samples of refuse molasses by the same method by which it was obtained from cane juice.

In one sample I determined the amounts of different forms of nitrogen according to a well known scheme of analysis with the following result :

|                                | Per cent. |
|--------------------------------|-----------|
| Nitrogen as free ammonia ..... | 0.011     |
| Nitrogen as albuminoids.....   | 0.126     |
| Nitrogen as peptones .....     | 0.050     |
| Nitrogen as amids.....         | 0.201     |
| Nitrogen as other forms .....  | 0.228     |
| Total nitrogen .....           | 0.616     |

Free ammonia was determined by distilling with magnesia free from carbonate, and albuminoids by precipitating with cupric hydroxide. The nitrogen designated peptones is that precipitated by phosphotungstic acid after the removal of free ammonia and albuminoids. In the case of cane juice and its products this precipitate does not contain peptone bodies, and its character will be treated in a future paper. After removal of these three forms of nitrogen, amids were determined by boiling for an hour with two per cent. sulphuric acid, neutralizing and distilling with magnesia free from carbonate and doubling the amount of ammoniacal nitrogen obtained for amid nitrogen. This method which is fairly accurate in the case of asparagin which gives up half its nitrogen as ammonia when boiled with dilute acids, is of no value in the case of glycocoll, so that the above analysis should read amids and other forms 0.429 per cent. instead of

|                  | Per cent. |
|------------------|-----------|
| Amids.....       | 0.201     |
| Other forms..... | 0.228     |

From a number of years' experience in working with cane juice, I am convinced that the formation of molasses is due to mechanical, rather than chemical, conditions, that the presence of viscous non-crystallizable bodies prevents the further crystallization of sugar by rendering the motion of the sugar molecules in the liquid difficult, and the mellassigenic action of crystallizable salts is very slight. A body such as glycocoll would then exert little effect on the crystallization of sugar one way or the other, especially as it exists in cane in such small

amounts, but it is likely that the proteid directly connected with glycocoll will be found to be highly melassigenic.

We have been in the habit of associating the so-called gums or viscous bodies in cane juice with the cellulose or non-nitrogenous constituents of the plant, but we may have to modify this view in the presence of a gelatin-yielding proteid peculiar to sugar-cane and allied plants.

LABORATORY OF KOHALA SUGAR CO.,  
KOHALA, HAWAII, H. I.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL  
OF APPLIED SCIENCE.]

## XXIX.—THE INFLUENCE OF ANTISEPTICS ON THE DIGESTION OF BLOOD FIBRIN BY PEPSIN IN A HYDRO-CHLORIC ACID SOLUTION.<sup>1</sup>

BY CHARLES F. MABERY AND LEO GOLDSMITH.

Received September 27, 1897.

WHILE it may be difficult to perform experiments on artificial digestion under conditions that approximate those of natural digestion in the body, it is possible to determine the influence of substances that exert a retarding influence on the normal chemical reactions which involve the solution of fibrin or albumin by pepsin in an acid solution. The retardation by certain artificial colors, oroline yellow, saffoline, and magenta, was studied by Weber,<sup>2</sup> and the influence of alcohol in different proportions, and other bodies by Chittenden and Mendel.

In a recent number of this Journal,<sup>3</sup> Frank D. Simons gave an account of results which he had obtained in studying the action on the digestive ferments of salicylic acid, formol, several dye-stuffs and essential oils.

In view of the stringent food laws that are everywhere recognized as necessary for the protection of the health and pecuniary interest of the consumer, the influence of adulterations commonly found in foodstuffs and in prepared foods should be well understood.

<sup>1</sup> The experiments described in this paper were made at my suggestion by Mr. Goldsmith, and they formed the subject of his thesis for the degree of Bachelor of Science. The paper was read at the meeting of the Cleveland Chemical Society, June, 1897.

C. F. M.

<sup>2</sup> This Journal, 18, 1092.

<sup>3</sup> *Ibid.*, 19, 744.

The results presented in this paper were obtained with alum, salicylic acid, boric acid, and formaline. The material used for digestion was blood fibrin separated by agitation in the ordinary way from fresh blood as soon as it was drawn from the steers. It was carefully separated into shreds as nearly as possible of uniform size and preserved in alcohol. For use it was thoroughly washed with water, spread out in thin layers on a glass plate, and dried at 100°. The digestive ferment was a scale pepsin, marked 1:3000, prepared by Armour & Co., of Chicago. In each of the following experiments twenty millimeters of pepsin was allowed to act in 100 cc. of a solution containing two-tenths of one per cent. of hydrochloric acid, on one gram of fibrin prepared as described above. The action was allowed to proceed for a definite time in a water-bath at 38°-40°, and the fibrin remaining after the experiment was stopped was removed by filtration, washed, dried at 100°, and weighed either on a Gooch filter or on a weighed paper filter. In every series of experiments the results were controlled by duplicate trials under the same conditions without the antiseptic.

#### EXPERIMENTS WITH ALUM.

##### *First Series. Time 4 Hours.*

| Weight alum.<br>Grams. | Weight undigested fibrin.<br>Grams. | Per cent. digested fibrin. |
|------------------------|-------------------------------------|----------------------------|
| 0.00                   | 0.0                                 | 100.00                     |
| 0.00                   | 0.0                                 | 100.00                     |
| 0.01                   | 0.0                                 | 100.00                     |
| 0.01                   | 0.0013                              | 99.87                      |
| 0.05                   | 0.0132                              | 98.68                      |
| 0.05                   | 0.0143                              | 98.57                      |
| 0.10                   | 0.0150                              | 98.50                      |
| 0.10                   | 0.0103                              | 98.37                      |
| 0.50                   | 0.0979                              | 90.21                      |
| 0.50                   | 0.0964                              | 91.36                      |
| 1.00                   | 0.1196                              | 89.04                      |
| 1.00                   | 0.1538                              | 84.62                      |
| 5.00                   | 0.7017                              | 29.83                      |
| 5.00                   | 0.7185                              | 28.15                      |

*Second Series. Time 6 Hours.*

|      |        |        |
|------|--------|--------|
| 0.00 | 0.00   | 100.00 |
| 0.00 | 0.0062 | 99.38  |
| 0.01 | 0.0102 | 98.98  |
| 0.01 | 0.0117 | 98.93  |
| 0.05 | 0.0155 | 98.45  |
| 0.05 | 0.0205 | 97.95  |
| 0.10 | 0.0162 | 98.38  |
| 0.10 | 0.0288 | 97.12  |
| 0.50 | 0.0600 | 94.00  |
| 0.50 | 0.0619 | 93.81  |
| 1.00 | 0.0813 | 91.87  |
| 1.00 | 0.0876 | 91.44  |

*Third Series. Time 4 Hours.*

|      |        |       |
|------|--------|-------|
| 0.00 | 0.0060 | 99.31 |
| 0.00 | 0.0070 | 99.30 |
| 0.00 | 0.0037 | 99.63 |
| 0.01 | 0.0103 | 98.97 |
| 0.01 | 0.0980 | 99.02 |
| 0.05 | 0.0235 | 97.65 |
| 0.05 | 0.0203 | 97.97 |
| 0.10 | 0.0349 | 96.51 |
| 0.10 | 0.0355 | 96.45 |
| 0.50 | 0.0798 | 92.02 |
| 0.50 | 0.0800 | 92.00 |
| 1.00 | 0.1780 | 82.40 |
| 1.00 | 0.1785 | 82.15 |
| 2.50 | 0.3472 | 65.28 |
| 2.50 | 0.3642 | 63.58 |

*Fourth Series. Time 3 4-5 Hours.*

|      |        |       |
|------|--------|-------|
| 0.00 | 0.0016 | 99.84 |
| 0.00 | 0.0025 | 99.75 |
| 0.00 | 0.0025 | 99.75 |
| 0.01 | 0.0031 | 99.69 |
| 0.01 | 0.0037 | 99.62 |
| 0.05 | 0.0070 | 99.30 |
| 0.05 | 0.0088 | 99.12 |
| 0.10 | 0.0247 | 99.53 |
| 0.10 | 0.0236 | 99.64 |
| 0.5  | 0.0810 | 97.90 |
| 0.5  | 0.0795 | 97.05 |
| 1.0  | 0.1797 | 91.03 |
| 1.0  | 0.1805 | 92.95 |
| 5.0  | 0.6094 | 82.06 |
| 5.0  | 0.6087 | 39.13 |

*Fifth Series. Time 3 Hours.*

|      |        |       |
|------|--------|-------|
| 0.0  | 0.0054 | 99.46 |
| 0.0  | 0.0063 | 99.37 |
| 0.02 | 0.0205 | 97.95 |
| 0.02 | 0.0192 | 98.02 |
| 0.10 | 0.0308 | 96.92 |
| 0.10 | 0.0345 | 96.55 |
| 0.20 | 0.0864 | 91.38 |
| 0.20 | 0.0755 | 92.45 |
| 1.00 | 0.7657 | 23.43 |
| 1.00 | 0.7540 | 24.60 |

In this last experiment equal weights of alum and sodium bicarbonate were used, and the weights are the weights of the mixtures.

The influence of the alum in retarding the digestive action of pepsin is clearly demonstrated by these results. Even with such small amounts as 0.01 gram, the influence is apparent, and it increases regularly and rapidly with larger proportions of alum. The duration of the experiment evidently affects the proportion of fibrin dissolved. In the fifth series the mixture of alum and sodium bicarbonate should reduce the acidity of the solution, thereby interfering with the normal condition of the digestive action.

For the purpose of testing the influence of alum under conditions of actual practice, two loaves of bread were prepared with the same weight of flour in each, one with alum baking powder containing alum, one part, sodium bicarbonate, one part, starch, one part; the other with a cream of tartar baking powder, composed of cream of tartar, two parts, sodium bicarbonate, one part, starch, one part. From the loaf after baking, the weight of alum was calculated. In each experiment sixty grams of bread were used, containing 0.75 gram of alum, or 1.5 grams cream of tartar, and in each trial the digestion was continued fifteen hours.

| Kind of bread.       | Weight bread<br>undigested.<br>Grams. | Weight bread<br>digested.<br>Per cent. |
|----------------------|---------------------------------------|--|
| Alum.....            | 30.78                                 | 48.70                                  |
| Alumi.....           | 29.85                                 | 50.25                                  |
| Cream of tartar..... | 22.34                                 | 62.76                                  |
| Cream of tartar..... | 23.28                                 | 60.12                                  |

From these results it is evident that alum has an appreciable effect upon the proportion of bread digested.

A series of experiments was made to ascertain the effect of salicylic acid on the function of digestion. But on account of the small solubility of the acid, the action could not be tried with larger quantities than two-tenths gram of the acid. With this quantity an appreciable retardation is indicated. The proportions and conditions of the experiments were the same as those of the preceding experiments with alum.

| Weight salicylic acid.<br>Gram. | Weight undigested fibrin.<br>Gram. | Digested fibrin.<br>Per cent. |
|---------------------------------|------------------------------------|-------------------------------|
| 0.0                             | 0.0276                             | 97.23                         |
| 0.0                             | 0.0384                             | 96.16                         |
| 0.05                            | 0.0484                             | 95.16                         |
| 0.05                            | 0.0317                             | 96.83                         |
| 0.20                            | 0.0671                             | 92.29                         |
| 0.20                            | 0.0635                             | 92.65                         |

#### EXPERIMENTS WITH BORIC ACID.

Boric acid seems to exert an influence on the rate of change, but the proportion of acid does not seem to be essential. In the following series of experiments the times of filtration were somewhat irregular, and the first three tests which were intended as a means of control, were not altogether satisfactory :

| Weight boric acid.<br>Gram. | Weight undigested fibrin.<br>Gram. | Digested fibrin.<br>Per cent. |
|-----------------------------|------------------------------------|-------------------------------|
| 0.0                         | 0.0393                             | 96.07                         |
| 0.0                         | 0.0290                             | 97.10                         |
| 0.0                         | 0.0155                             | 98.45                         |
| 0.05                        | 0.0718                             | 92.82                         |
| 0.05                        | 0.0754                             | 92.46                         |
| 0.10                        | 0.0447                             | 95.53                         |
| 0.10                        | 0.0504                             | 94.46                         |
| 0.30                        | 0.0620                             | 93.80                         |
| 0.30                        | 0.0380                             | 96.20                         |

#### EXPERIMENTS WITH FORMALINE.

The influence of formaline seems to be more marked than that of boric acid. In general the action is greater with the increase in weight of the antiseptic :

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| Weight formaline.<br>Gram. | Weight undigested fibrin.<br>Gram. | Digested fibrin.<br>Per cent. |
|----------------------------|------------------------------------|-------------------------------|
| 0.00                       | 0.0393                             | 96.07                         |
| 0.00                       | 0.0290                             | 97.10                         |
| 0.00                       | 0.0155                             | 98.45                         |
| 0.05                       | 0.0585                             | 94.15                         |
| 0.05                       | 0.0413                             | 95.87                         |
| 0.10                       | 0.0905                             | 90.95                         |
| 0.10                       | 0.0752                             | 92.48                         |
| 0.30                       | 0.1101                             | 80.99                         |
| 0.30                       | 0.1045                             | 89.55                         |

While all the substances tested in these experiments show some influence on the digestive action of pepsin, only alum exhibits a marked effect. Although it is not possible, on account of the complex conditions existing in the stomach, to draw any conclusions from these results on what should take place in natural digestion, it would seem possible to conduct series of experiments on digestion within the stomach, introducing into the food suitable proportions of the antiseptics, and to determine the effects on the blood, and in other directions within the system. But such experiments are within the domain of physiological chemistry.

## REVIEW.

## SOME RECORDS OF RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

During very recent years, progress in industrial chemistry, as in practically every field of human activity, has been peculiarly marked. Competition between manufacturers, depression in trade and commerce from various causes, the opening of new channels of consumption, have all done their share to establish that necessity, which from all time, has been such a vigorous stimulant to investigation and invention, and the results, as a rule, have been proportional to the needs presented. It is apparent in the advances being made that there is an increasing recognition of the value of rational over empirical work and of the effort of carefully educated men over that of men who, ignorant of the cardinal and fundamental principles of the processes they control, grope darkly after the ends they would attain. And so for us here, and at the present time one of the most important signs of progress is to be found in the increasing and exacting interest being manifested in all the leading manufacturing countries of the world in the education of technologists, and the im-

provement in means to that end. Germany and England have been particularly aroused regarding their special needs in this direction, and have been forced to it by the intense competition existing between the two countries in the different fields of industrial chemical activity. The education of technical chemists has therefore been the theme of discussion in the legislative halls, in the conventions of technologists and manufacturers, and in the meetings of the scientific and educational associations, and the feeling almost universally expressed is to the effect that the work of education should be made more thorough and exacting, and that it should be carried up from the technical high schools to the universities, and that the same care should be applied to technical instruction as is considered necessary in university work. So Dr. Böttlinger, addressing the House of Delegates of Germany, urges upon the ministry the establishment of departments of technical chemistry with the necessary corps of instructors in the university and state examination of all technical chemists as soon as they shall have been graduated. Dr. Althoff, replying to Dr. Böttlinger, calls attention to the extension of technical chemical work in the different institutions and particularly in the University of Berlin, and at the same time he calls attention to the more thorough study of physics, theoretical and applied, as it is particularly carried on in Göttingen. Dr. Lippmann declares that if progress in the chemical industries is to continue, the facilities for the education of technical chemists, (this class constituting ninety-five per cent. of the about 4,000 chemists in Germany), must be greatly improved. Similar ideas have been expressed by Professor Wichelhaus, Dr. Duisberg, Dr. Ostwald, and others of highest authority in both educational and technical fields. Dr. F. Fischer has treated the subject most exhaustively in a paper entitled "The Study of Technical Chemistry in the Universities and Technical High Schools of Germany and the Examination of Chemists."<sup>1</sup>

A congress, devoted to technical education, was held in London, June 17, 1897, the Duke of Devonshire presiding. In his opening address he compared the technical schools of England with those of other countries, extolling the organization and work of the technical schools of France and the Realschulen of Germany, and enlarged upon the value of thorough preparatory training of those who will enter the field of technical work with prospects of success. This Congress was likewise addressed by Dr. O. N. Witt, of Berlin, Dr. Lunge, of Zurich, and Dr. J. H. Gladstone, of London.

<sup>1</sup> The subject was further eloquently discussed in the general meeting during the past summer of the German Electro-Chemical Society by Dr. Ostwald, Prof. v. Baeyer, Dr. Böttlinger, Dr. Holtz, and others. The discussion is worthy of careful study.

Responding to the general demand, the new University of Brussels has established in the Gährungs Institut, under the direction of Dr. J. Effront, a summer course of study on subjects relating specially to the fermentation industries. It consists of lectures by eminent authorities in the different departments, accompanied by illustrative exercises in the laboratories for analytical chemistry, bacteriology, yeast culture and fermentation.

In our own country, while the demand is probably not so imminent, the possibilities of it have been most wisely foreseen by the directors of many of the educational institutions, and the extension of study to the applications of the principles of chemistry and physics is gratifying. In the East this is particularly manifest in the Massachusetts Institute of Technology, in Harvard University, Columbia University, Cornell University, and the University of Pennsylvania; and the institutions located west of the Alleghanies are working in the same direction with excellent results.

These are, it seems to me, the most important signs of fundamental progress in industrial chemistry that can be imagined or considered. We must all accept the expressed views regarding the better and more thorough education of the young men upon whom the responsibility for further progress must fall. For myself I have come to feel most acutely this necessity of our times and the desirability of a supply of young men who have had training not in the hurry of a year or two to make chemists who are analysts merely, and more frequently very indifferent analysts at that, but of those who have had the most careful training in the fundamental principles of the science, the physical relations of the elements and compounds, the thermal and electrical relations, the great theories upon which all productive practical work must be based. In many respects, heretofore, the tendency to specialization has been too marked and to the detriment of the all-round training necessary to effective work. Men carefully trained first in the fundamental principles and theories and then in the practice of observation and investigation are better able to apply themselves to specialties, than those trained as specialists are to meet the problems and difficulties which are likely to come to them in the conditions and situations in which they are sure, at one time or another, to find themselves. It seems to me, therefore, that the demand of the present time, and that of the immediate future, can be met only by broadly educated men; by men who have been trained not only in chemistry of itself, but in the great principles of physics as well. A good technical chemist must first of all be a good and thoroughly educated chemist; after that, to obtain the highest success in

this country, he must be educated in the principles of engineering; the production and applications of heat; the production and applications of electricity; the transmission of power; the movement of liquids; in general the means whereby the reactions of chemistry, which he may be called upon to apply, may be carried out in a large way. If the young men are to occupy commanding positions in the great chemical works, they must have preparation in these lines before they leave the educational institutions or they must acquire it after they have been graduated from them and have entered upon their life work. I agree with Dr. Duisberg, that whenever it is possible it is better to employ a chemist for chemical work, and an engineer for the engineering work in establishments where the best organization is to prevail, but in this country where the industries are in most cases not so largely developed as in Germany or England, and where beginnings have still to be made, the chemist will in very many cases be compelled to do his own engineering, even as in many cases the engineer must be his own chemist. We need, therefore, chemical engineers, and these in the nature of the requirements must be broadly and thoroughly educated men. While they must be trained for the work of the research laboratories, which are being organized in connection with many of the great industries, they must likewise be prepared to put into practical operation in a large way the results of the researches they have been called upon to make.

In this connection I cannot refrain from urging upon educators the importance of impressing upon young men that the controlling principle of successful work is the search for and establishment of truth; that honesty is after all the foundation of true progress; that absolute accuracy and personal responsibility are the prime necessities, and will be as firmly exacted in the valuation of a commercial product as it must be in the determination of an atomic weight.

It is not my purpose in this paper to enter further into the discussion of this great, interesting and absorbing question. I touch upon it by way of introduction, because of the great progress the present and continued agitation of it indicates, and the enormously important results which in the near future must flow from it.

Another important manifestation of progress in industrial chemistry is to be seen in the organization of the series of International Congresses of Applied Chemistry to be held once in two years in the different capitals of the world. The first of the series was held in Brussels in 1894, and the second was held in Paris last year. The latter was organized under the direction of the Association des Chimistes de Sucrerie et de Distillerie de

France et des Colonies, and met in Paris from July 27 to August 7, 1896, with over one thousand delegates in attendance from different countries, and nearly every branch of chemical industry represented. The several sections into which the congress was divided held more than sixty separate sessions, and it is stated that the report of the proceedings will require three volumes of at least 500 pages each.

One of the useful results of the work of the congress was the adoption of the proposition of the Verein Deutscher Chemiker, regarding the preparation and standardization of chemical measures. Two committees, one French, and another German, were appointed to consider this subject, and before the conclusion of their labors they are to meet together to prepare a report to be delivered and discussed in the next congress to be held in Vienna in 1898.

Most important results may be expected to flow from the labors of these eminent authorities, and the establishment of the committee illustrates most forcibly the demand for exactness and accuracy in technical work.

No less important as indications and records of industrial progress are the expositions of the products which are being held from time to time in different parts of the world. The Berlin Exposition held during the past year is an excellent illustration of this fact and the report of Dr. O. N. Witt upon it may be studied with profit by those who would gain a good knowledge of the progress of industrial chemistry in Germany as illustrated in the commercial products and manufacturing apparatus there exhibited. He describes the means for the use of liquid and pulverized fuel; the utilization of gas-house wastes for acid manufacture and as an accompaniment of this process the preliminary recovery of the ammonia and cyanides from the crude product; the production of material for the Welsbach mantles in which so great progress has been made during the past few years; compressed gases for various uses; the production of five chemicals; the persulphates and the admixture of these new and useful substances with the cyanides to be used in gold extraction; colors and organic disinfectants and remedies; fats and candles; soaps; artificial ethereal oils; and other substances of interest to chemists and of value to the industries. The information offered concerning the products exhibited and the principles upon which their preparation is based is extensive and the entire paper is characteristic of its author.

In like manner the report of Dr. Oppler on the department of chemical industries of the Bavarian Landesausstellung held in Nürnberg and opened May 14, 1896, is of most interesting value. The distribution of the exhibitors in this department is

an indication of the character of the information offered in the report of Dr. Oppler and the numbers in each class respectively are as follows : Salines, 4 ; heavy chemicals, 2 ; ordinary chemical preparations, 16 ; colors, 21 ; aniline colors, 1 ; explosives, 3 ; matches, 4 ; artificial fertilizers and glue, 17 ; resins and pitch, 6 ; soap-boiling and perfumery, 16 ; stearin and wax candles, 11 ; ethereal oils and petroleum distillates, 2 ; varnish lacquer and cements, 8 ; asphalt and roof covering, 2 ; rubber manufactures, 4 ; impregnating, 1 ; mineral water manufactures, 4.

That this exhibition should have been important was to be expected from the fact that in Bavaria, of a total population of 5,268,761, at least 685,298 are employed in the industries ; that the Badische Anilin and Soda Fabrik in Ludwigshafen, which employed last year 4,800 persons including 100 educated chemists and 30 trained engineers, is to be included in the works represented. Besides the products of the truly chemical industries, metallurgical products, fuels and cements were largely represented and are exhaustively treated by Dr. Oppler in his report.<sup>1</sup>

The further register of the progress attained in the industries is to be found as well set forth in the literature of patents of invention as in other published matter. For it must be acknowledged that however much of careful work may be done in the research laboratories of the great industrial establishments or however important may be the immediate results of the application of new processes, the knowledge acquired finds its way to the published records but slowly and is generally held back because of the necessities of the active competition involved in the struggle for commercial supremacy. The protection afforded by the patent laws serves therefore a doubly useful purpose : that of preserving to the inventor or investigator the commercial results of his labor, and of bringing before the world without delay the truths which have been developed to serve as suggestion or incentive in further efforts in like or different directions. It will profit us therefore to consider briefly some of the developments which in this way the past year has brought forth.

It would be impossible in the time which could reasonably be allotted to such a paper to cover the entire field of industrial chemical activity and we must therefore be content with a limited scope. Some of the departments can be treated intelligently only by specialists working in them ; and this applies particularly to the carbon compounds used as colors and dyes, as disinfectants and as remedial agents, the progress in the production of which has been enormous and most rapid. It is also true of the fermentation industries which have been so materially advanced by

<sup>1</sup> The exhibitions of Brussels and Leipzig have been very important and must have a marked influence upon all departments of industry and those involving the applications of chemistry must share the impulse. Valuable reports will doubtless be made of these two exhibitions.

biology and biochemistry; of the clay and cement industries which have been so much stimulated from the engineering sides. In metallurgy besides the further development of the basic process for manufacture of steel and the utilization of its wastes, the electrolytic production of aluminum, the electrolytic refining of the heavy metals as lead, copper, silver, and gold, considerable activity has been shown in the development of the cyanide and other processes for the extraction of gold from low grade ores by lixiviation. The cyanide process of MacArthur and Forrest has received special attention and has been improved by the addition of various agents to the solution for lixiviation to render it more active. Keith adds mercuric cyanide equal in weight to half that of the alkaline cyanide used and claims that the mixed cyanides act more rapidly and effectively than the alkaline cyanide alone. Mactear proposes the use of cyanuric acid equivalent to about five per cent. of the weight of potassium cyanide and to produce the compound within the solution by adding hypochlorite or hypobromite thereto. He claims that the solvent action of the cyanide is increased and that saving of cyanide is effected by reducing its action upon the base substances in the ore. The Chemische Fabrik auf Actien, recognizing that oxidation is necessary to the effective reaction between gold and the cyanide, and recognizing the disadvantages and losses attending the use of the metallic peroxides, permanganates, ferricyanides and hypochlorites because of their power to oxidize the cyanides to cyanates, have found that the persulphates, while they have no oxidizing action upon the cyanide even with considerable concentration and a temperature as high as 45° C. when mixed with the cyanides, render them peculiarly active as solvents for gold and silver. The solution is more active in the presence of free alkali which serves to combine with the acid liberated by the decomposition of the persulphate, and to form a compound which may be stored, transported and readily used, the company mix together ten parts of potash, forty parts of potassium persulphate and fifty parts of potassium cyanide. The mixture is dissolved in water in the usual way and in the usual proportions.

The same company have found that the nitro and nitroso-carbon compounds and the salts of their sulphonic acids have a similar intensifying influence upon the solvent power of the cyanides. For instance the addition of nitrobenzene to the cyanide solution is claimed to make it act from forty to fifty times as rapidly as the plain solution of equal strength.

For ores, to the treatment of which the cyanide process is not applicable, Lodge and Cassel and Hinman propose the use of weak solutions of bromine. A solution containing 0.15 to 0.25

per cent. of bromine is suggested and digestion of the ore with the solution is to be continued about two hours before final lixiviation. It is claimed that the solvent power of bromine is greater than that of chlorine and that it is further more effective because it carries less of baser metal into solution.

Endeavor in the separation of zinc from its ores and admixture with other metals has been active, and the results secured by Siemens and Halske seem to be of practical value. These authorities leach the ore containing zinc oxide with a solution of aluminum sulphate whereby basic aluminum sulphate is produced and zinc is carried into solution as the sulphate. The leach is electrolyzed when zinc is deposited at the cathode and the aluminum sulphate is regenerated at the anode. Kellner leaches the ore with a caustic solution, dissolving the oxide, obtaining a leach from which the metal may be extracted by well-known methods. And Mond modifies it by placing within the solution some sodium amalgam, plunging into the amalgam a rod of metal electronegative thereto, when the zinc is deposited on the rod.

Mond has further developed his process for the extraction of nickel dependent upon the production of the volatile carbonyl compound of the metal. In practice the metal is first reduced in the ore by means of hydrogen and the cooled ore transferred to the volatilizing chamber where, descending from one tray to another, it meets an ascending current of carbon monoxide gas. The carbonyl compound is carried to an adjoining chamber where decomposition takes place and the metal is deposited.

The example of Whitehead in the preparation of tellurium on a comparatively large scale has been followed by Farbaky in Scheminitz who has succeeded in obtaining an ingot of 820 grams of the purified product.

Hilbert and Frank have improved upon the production of phosphorus in that they avoid the intermediate preparation of the crude material by heating the latter in an electric furnace similar to that used for carbides. For instance ordinary calcium phosphate is ground up with carbon and the mixture heated in a properly constructed furnace. Reduction promptly occurs, calcium carbide is formed, and phosphorus and carbon monoxide liberated. Aluminum phosphate serves as well.

In the commercial production of the carbides some progress has been made. The production of the silicon compound, carborundum, is reported to have amounted in 1896 to 1,191,000 pounds of the crystalline variety. The amorphous product which accompanies the crystalline variety has thus far been of little or no commercial value but it has been suggested as a substitute for ferrosilicon in steel manufacture. It has been estimated that Ger-

many alone could use annually 2,500 tons of the product and an endeavor will be made to supply it.

The brilliant work of Moissan in the application of the electric furnace to the production of the carbides has brought forth among many others the titanium carbide which excels in hardness all known substances and which without great delay will probably become a commercial product.

The production and application of calcium carbide are extending. The Neuhausen Aluminum Company have established new works at Rheinfelden and the electro-chemical works at Bitterfeld have acquired land for the same purpose. The former company it is said will produce carbide at a cost below forty pfennigs per kilogram, a price scarcely encouraging. In spite of the extension of the manufacture comparatively little progress has been made in the process used beyond the mechanical appliances for making it continuous. The reduction in the cost of the product must be effected by reducing the cost of the power used.

What is true concerning the carbide is likewise true of the acetylene gas produced from it. Hundreds of devices have been made for liberating the gas for use in various ways all differing but little in principle and only as regards mechanical construction. Compared with coal gas and taking into account its illuminating capacity when used alone or mixed with air it is probably no more expensive but the prejudice prevailing regarding its sensitive character and the consequent danger attending its use in spite of the official reports regarding this quality will deter its wide application. Experiments with the gas in engines gave results unfavorable to its use in that way.

For use to enrich coal gas for illuminating, acetylene has proved less effective than benzene with which at the present time at least five per cent. of the gas used in Germany is improved. The declining cost of benzene due to its increasing recovery from coke-oven gases makes it available for this and many other uses from which, on account of cost, it has heretofore been excluded. It has been found particularly effective in the crude state when mixed with spirit for use in the incandescent spirit lamp. Experiment has shown that spirit mixture containing fifteen per cent. of xylene gives a temperature of 6,700° C. If the crude benzene in the spirit mixture be increased to 33½ per cent. it is stated that it may be used as a substitute for petroleum in coal-oil lamps.

In Germany the process of extracting the benzene from the coke-oven gases has consisted in passing the latter through a tower against a finely divided stream of high boiling-point hydrocarbon oil and subsequently separating the benzene by fractional distillation, while the oil is cooled and returned to the tower. The quantity so produced up to the beginning of 1896 amounted

annually to from 4,500 to 6,000 tons and it is estimated that if the production should increase according to expectation it should reach as high as 80,000 tons.

Heinzerling proposes to recover benzene by compressing and cooling the gas and to this end the compressed gas is made to pass through a series of pipes which are cooled by a current of the gas from an expansion cylinder whereby a temperature of  $-70^{\circ}$  to  $-80^{\circ}$  C. is produced within the tubes. Two sets of condensing tubes are used alternately and the moisture and dust, which would seriously interfere with the process, are carefully removed. With a consumption of 240 horse-power produced from gas from the ovens 60,000 cubic meters of gas yielding 1,200 kilos of benzene are daily condensed.

Nikoforow has attempted to break up petroleum and its residues by repeated fractional distillation at temperatures ranging from  $550^{\circ}$  C. at ordinary pressures to  $700^{\circ}$  C. and even  $1,200^{\circ}$  C., with pressures up to two atmospheres, securing a yield of benzene equal to about twelve per cent. of the material used.

Mabery and Byerly convert petroleum residues into asphalt by passing a current of air through the heated mass. The distillation is begun at  $450^{\circ}$  C. and is continued until a temperature of  $650^{\circ}$  C. is attained. One of the products secured is said to be similar in its qualities to the natural product gilsonite.

In the desulphurization of petroleums Heussler proposes heating them with about five per cent. of aluminum chloride for twenty-four hours. At the end of the period, if the exhalation of gaseous products has ceased, the oil is distilled. Better results were obtained by doubling the quantity of the chloride and continuing the heating to 120 hours. Hinrici finds that equally good results may be obtained, with as great economy, by heating the crude oil with an equal weight of oil of vitriol of  $66^{\circ}$  B. With crude oil containing one and two-tenths per cent. sulphur he obtained a solar oil distillate containing 0.063 per cent. of sulphur. At this rate he finds the acid no more expensive than the chloride and equally effective.

Many of us will remember that somewhat more than a year ago, Nikodem Caro published the results of his experiments in the preparation of alcohol from acetylene after the reactions established by Berthelot, obtaining a yield so far below what theory requires, as to render the reaction a practically hopeless one. The production of synthetic alcohol has been revived by Fritsche who has made use of the reaction discovered by Faraday and subsequently studied by Berthelot to whom it has often been credited. Attempts had been made successively by Berthelot, Cattelle and Mallet, to extract the ethylene from coal-gas and convert it into alcohol but all failed because of the presence of other

substances which were extracted at the same time and interfered with the subsequent reactions. But since the establishment of the coke-ovens and the extraction of the tar, ammonia, and benzene so completely from the gas Fritsche concluded that the ethylene could be profitably recovered and utilized. The eighteen coking establishments of Germany using a million and a half tons of coal, yielding gas containing one to one and eight-tenths per cent. of its volume of ethylene should represent an annual possible production of 95,000 hectoliters, (nearly 2,500,000 gallons) of alcohol. The large number of experiments made showed that complete absorption of ethylene may be effected by strong sulphuric acid, and when the acid is kept at 140° C. the absorption is very rapid and may be carried to a concentration of 50 per cent. of the compound produced without exhausting the absorbing power, so that 100 pounds of vitriol will serve for the absorption of 14 kilos of ethylene which will yield 18 kilos of alcohol. For the production of 100 kilos of alcohol, 350 kilos of 66° B. sulphuric acid will be required and for the complete recovery of the alcohol this must be mixed with at least 500 liters of water. The water is subsequently evaporated and the acid recovered.

Fritsche expresses doubt if, at the present cost of alcohol, the process, which gives yields very close to theory, may become profitable. But for the production of such alcohol derivatives as potassium ethyl-sulphate, ether and acetic ether, etc., he considers it has some possibilities.<sup>1</sup>

In the manufacture of the acids and the bleaching compounds some advances have been made, but in this department of industry progress is necessarily slow. Attempts have been made to replace the lead chambers in vitriol manufacture by stoneware towers, but thus far the adoption of the improvements claimed has not been extensive. The demands of the color and explosives manufacturers for pure nitric acid of high concentration have naturally stimulated endeavor to meet them and with good results. Dr. Hart's condenser with its return connections has already found very extensive application and has proven most effective in yielding a high grade and pure product. Dieterle and Rohrmann endeavor to attain the same end by passing a current of air into the distilling chamber and providing return connections in the condensing coils to a side pipe for the escape of the air carrying the halogen and other impurities. The nitrous compounds are said to be oxidized to nitric acid and the high grade distillate to be therefore free from these troublesome substances. Dreyfus decomposes alkali nitrates at a temperature carefully regulated at 170° to 190° C. in a vessel in which a vacuum may

<sup>1</sup> Fritsche has since patented a process for manufacture of ether from ethylene and claims that practically theoretical results may be obtained.

be maintained. Main and Stevenson heat a nitrate and manganese dioxide together in a muffle and convey the nitrous compounds liberated to an oxidizing tower fed with dilute nitric acid. The nitric acid produced is finally distilled from strong sulphuric acid, yielding a product of high degree and the sulphuric acid is concentrated by evaporation for use in subsequent charges. The residue in the muffle is heated with steam, and sodium hydroxide and manganese dioxide recovered.

Valentiner recovers the nitric acid from waste acids by distilling it from strong sulphuric acid in a vacuum. He states that if a mixture of 800 kilos of strong sulphuric acid and 1,200 kilos of impure nitric acid of 1.40 sp. gr. be distilled *in vacuo* so that the temperature may not exceed 100° C., all the water and impurities will be held back and nitric acid of 94 to 96 per cent. of monohydrate will be obtained.

The Verein Chemischer Fabriken likewise distil the acid from strong vitriol. From a properly constructed vessel containing sulphuric acid the nitric acid vapors are carried into a tower fed with water heated to 85° C. and from here they pass to the cooling condenser. The warm water absorbs the impurities and returns them to the still and the pure acid issuing from the condenser is said to have a strength of at least 94°.

Jung and Steuer undertake to recover hydrochloric acid by a somewhat round-about process from the calcium chloride of the ammonia soda process. The properly concentrated chloride liquor is mixed with copper sulphate to produce double decomposition. The cupric chloride separated from the calcium sulphate is decomposed by hydrogen sulphide. The copper sulphide separated from the hydrochloric acid is exposed to the air in thin layers to be oxidized to sulphate for subsequent use in the process while the calcium sulphate is heated with carbon, in furnaces, to reduce it to sulphide, which, in turn, may be treated for sulphur by the Chance process. It is extremely questionable if the hydrochloric acid can be obtained in this way entirely free from lime salts, but the inventors suggest that these will not interfere particularly when the acid is to be used for the generation of chlorine by the Weldon process.

In view of the rapid extension of the production of chlorine by electrolysis, the reaction, occurring when aqueous vapor and chlorine are led over glowing carbon, producing hydrochloric acid and carbon monoxide, acquires a higher interest. It is possible that the process based upon this reaction may yet prove profitable, and certainly it will be free from the growing objection of the old process, that it will leave behind no residue of cumbersome sodium salts.

In the generation of chlorine from hydrochloric acid, a great

deal of experiment and investigation have been carried on. The improvement of the Deacon process by passing air along with the acid gas, Mond's substitution of nickel for the copper of the Deacon process, and the various modifications of the reaction between nitric acid and hydrochloric acid have all had their supporters. The latter reaction has had the largest share of attention, but in spite of all the thought and energy which seem to have been devoted to it, the promise for its future is not brilliant. All the processes and forms of apparatus devised for carrying out the reaction depend upon bringing the nitrosyl chloride into proper contact with vitriol. The process and apparatus seem to have the merit of greater simplicity, at least, than the others described, and the essential part thereof consists in perfecting the oxidation of the hydrochloric acid and the decomposition and removal of the nitrous compounds by systematically subjecting the gas alternately to the action of nitric acid and hot sulphuric acid. To effect this they arrange two vertical towers, each divided into compartments by diaphragms with hydraulic seals. A stream of nitric acid is made to flow downward through one tower and hot sulphuric acid to descend through the other. Gas from the decomposing apparatus and containing nitrous compounds is introduced to the bottom of the lower compartment of the nitric acid tower and passes from the top of this to the bottom of the lower compartment of the vitriol tower. From the top of this, in turn, the gas passes to the bottom of the next upper compartment of the nitric acid tower, then from the upper part of this compartment back to the bottom of the second compartment of the vitriol towers and so by zigzag course from one to the other, until it finally passes out from the top of the vitriol tower dry and free from hydrochloric acid and nitrous compounds. The acids used in the towers are regenerated for use in subsequent charges.

As before stated, this differs practically only in the mechanical arrangement for effecting the oxidation and the purification of the chlorine gas, and is therefore similar to the processes of the Wallis chlorine syndicate, of Sadter and Wilson, Scott and Vogt, Verein Chemische Fabriken zu Mannheim, Krause, and others, which have been described within the past year and a half. The complicated character of the apparatus required, the difficulty in moving the corrosive gas, the losses of nitric acid, all conspire against the extensive application of any of these processes in competition with the new electrolytic processes for the same purpose. The latter are being adopted with enormous rapidity, as may be gathered from some statistics from Germany for 1895 and 1896. Thus, from January 1 to the end of September, 1896, the imports of chloride of lime were 3,342 tons, and the exports 50,549 tons; while for the corresponding

period of 1895 the imports were 10,232 tons, and the exports 23,636 tons. In Austria, it is stated, that works using 200 horse power are in operation, and those requiring 3,000 horse power in process of erection. In England these processes have been received with peculiar favor and thousands of horse power are being consumed in the works devoted to them. At Saltville, Va., the Matthieson Alkali Company have made a beginning and have projected works to be erected at Niagara Falls covering twenty acres of ground. These works, when completed, will use the Castner process, and employ 150 men and 2,000 horse power.

The methods which have been found most effective and acceptable are those without diaphragms, like that of Castner and Kellner, and those with diaphragms similar to that of Hargreaves and Bird. Thus far the former have had the widest application, although it is claimed that the Hargreaves cell can be operated with a lower consumption of power. The difficulties in the operation of both kinds are, however, being rapidly overcome, and we are likely, in the near future, to be called upon to record the entire replacement of the old chlorine and soda plants by those operating the electrolytic processes.

Before leaving the subject of electrolysis in the production of bleaching compounds, we may not overlook the new and interesting peroxidized substances—persulphates and percarbonates—which bid fair to replace many of the well-known oxidizing and bleaching agents.

Persulphuric acid and the persulphates are produced by the electrolysis, respectively, of the free acid or the acid salts. The most useful, however, are the potassium, ammonium, and aluminum salts, that of ammonium being the most stable. In like manner Constan and von Hansen produce the potassium percarbonate by electrolyzing a saturated solution of potassium carbonate, kept at a temperature of  $-10^{\circ}$  to  $-15^{\circ}$  C. Platinum electrodes are used in a cell with a diaphragm and the product obtained, which decomposes readily, must be protected from heat and dried quickly. It is comparatively stable in iced water, but in warm water it breaks up with production of free oxygen. Both classes of salts may be used as oxidizing agents, and the persulphates, as already stated, have been recommended for use in the cyanide gold extraction process, to intensify the solvent action of the cyanide solution.

Wolfenstein finds that hydrogen peroxide solution, if free from certain impurities, may be concentrated by ordinary evaporation to about fifty per cent. To concentrate it further it may be extracted with a substance, like ether, insoluble in water. After removal of ether the product may be distilled in a vacuum

of sixty-eight mm. and a temperature of  $84^{\circ}$ - $85^{\circ}$  C., yielding a distillate containing ninety-nine per cent. of the peroxide.

It is probably true that in no field of chemical industry has greater activity been manifested than in the production of the compounds of nitrogen, and particularly ammonia and the cyanides. The increasing demands of agriculture, the manufacture of the various nitro compounds for colors and explosives, and the new gold extraction processes, have long served to stimulate the search for new sources of combined nitrogen and the effort expended is beginning to bear fruit. Heretofore, the principal known sources of combined nitrogen have been animal or other organic matters, and coal and the niter beds of South America. The latter has been an almost constant source of supply. That from animal matter has grown with the growth of the great meat-packing industries and the recovery of their waste products, while the improvements continually being made in the gas and coking industries would seem of themselves almost capable of meeting the demands. It is interesting in this connection to compare the English statistics for sulphate of ammonia production in 1886 and 1895, respectively.

|                   | 1886.<br>Tons. | 1895.<br>Tons. |
|-------------------|----------------|----------------|
| Gas works.....    | 82,480         | 119,645        |
| Shale works ..... | 18,090         | 38,335         |
| Iron works .....  | 3,950          | 14,588         |
| Coke works.....   | 2,100          | 7,083          |

The iron works ammonia is produced largely in Scotland, where, it is stated, as much as two and a quarter million dollars are invested in its recovery.

Hagenstock, of Dalhausen, states that Rhenish Westphalia alone produces annually 6,000,000 tons of coke, using 8,000,000 tons of coal. On the basis of the recovery of ammonium sulphate, equal to one per cent. the weight of the coal, the amount annually recovered should be 80,000 tons, worth \$4,000,000. Knublauch gives some interesting figures regarding the distribution of nitrogen in the distillation of coal and finds that about fifty per cent. of the nitrogen remains in the coke, thirty per cent. remains in the gas, twelve to fourteen per cent. is converted into ammonia (corresponding with 10.55 pounds sulphate of ammonia per ton), nearly two per cent. into hydrocyanic acid (equivalent to 1.42 pounds ferrocyanide per ton), while one and a half per cent. is found in the nitrogen bases in the tar. On the basis of a yield of 0.20 to 0.25 per cent. of the weight of the coal, the 1,000,000 of coal, which he estimates is daily consumed in the gas-works and coke-ovens in the world, the sulphate available should amount to 10,000 to 12,000 tons. Yet Truchot, quoting Legrand, declares that Belgium uses in agriculture but

one-sixth, Germany one thirty-sixth, France one fifty-fourth, and England one sixty-sixth the nitrogenous manures they might use with advantage. If this estimate of Legrand be correct it is easy to see that the possible demand is far from being met at the present time.

The indirect utilization of atmospheric nitrogen by vegetation has now been fully established. Von Beyerrinck, Hellriegel, Wilfarth, Nobbe, and others, find the most important agent in this connection to be the bacteria of the root nodules of leguminous plants. And Nobbe and Heltner find that these nitrogen-fixing bacteria, when introduced to soils free from them and unsuited to the cultivation of leguminous plants, produce in the roots of such plants nodules or tubercles, in which fixation of free nitrogen and its conversion into assimilable forms is effected. Soil wanting in assimilable nitrogen, and therefore practically sterile, becomes fruitful and will produce good leguminous crops when inoculated with the bacteria.

The bacteria are produced in agar gelatine containing sugar and asparagin or the green substance of the plant. The culture medium, when saturated, may be dissolved in water and so be used to moisten the seed, or it may be mixed with dry earth, which is sown broadcast. The firm of Meister, Lucius & Brünning, in Höchst on the Main, have undertaken to produce cultures of the bacteria commercially and supply them in form convenient for transportation, preservation, and distribution. The cultures are enclosed and marketed in small bottles, each containing sufficient to inoculate half an acre of ground. The success of the new industry remains to be established.

In the production of ammonia from sources other than those mentioned, Sternberg proposes the ignition of such organic matters as sugar-house waste, with alkali aluminate made by melting together lime, crude potash, and bauxite or clay. This, finely ground, is mixed with the organic waste, such as molasses, and charged to the top of a vertical retort so arranged that the gases generated may be drawn over the hotter charge at the bottom. From time to time the aluminate is drawn off at the bottom to be used again, and fresh material is charged to the retort at the top. Nitrogenous gases may likewise be passed over the hot material for ammonia production. This process has elsewhere been credited to F. O. Matthieson.

Raschen and Brock propose passing a mixture of nitrosyl chloride and hydrogen over heated platinized asbestos whereby, in presence of some excess of hydrogen, reduction is effected and ammonium chloride is produced. The vapor is conducted into a chamber maintained at 100° C., where the salt is deposited. In like manner it is stated that nitrogen oxides may be reduced to ammonia.

Lord Rayleigh has lately made a study of the oxidation of free nitrogen under the influence of the electric spark. He made a large number of experiments and obtained the best results by confining in a flask a mixture of eleven parts of pure oxygen and nine parts of air, passing through the mixture a spark from a current of forty amperes and 8,000 volts. In practice he forced a solution of potash into the flask in such a way that its walls were constantly washed, the liquor being kept cool, and passed the mixed gases through the flask while the current was in operation. His results showed the efficiency to be equal to twenty-five cc. of absorption per Watt hour.

Following the same line of thought, Siemens and Halske claim that when air or oxygen and nitrogen are mixed with ammonia and subjected to the influence of the silent electrical discharge a profitable yield of ammonium nitrate may be obtained. It is important to the efficiency of the reaction that the air or gases and the ammonia shall be perfectly dry before they enter the apparatus, and that the air be previously ozonized. In practice the dried air and ammonia gas in proper proportions, which are found to be one volume of air and 0.01 to 0.02 volume of ammonia are passed slowly through an apparatus similar to that for producing ozone, and it is claimed that if the precautions described are carefully observed, the whole of the ammonia will be converted into ammonium nitrate. From the results obtained by Lord Rayleigh and by Siemens and Halske, it would seem that the presence of an alkaline substance to combine with the oxides at the instant of their formation is necessary to the reaction.

Since the discovery of argon and the application of magnesium and lithium to the removal of the nitrogen from the deoxidized air by the formation of the nitrides, considerable attention has been devoted to the commercial production of these interesting compounds. Rossel and Franck studied the subject experimentally following the suggestion of Winkler that the combination of magnesium and nitrogen is favored by the presence of an indifferent substance to prevent oxidation, heat together at red heat in an open crucible, a mixture of calcium carbide and magnesium powder, and find that the magnesium is practically all converted to nitride. They state further that under similar conditions aluminum, zinc, and iron will take up nitrogen.

Mehner, and likewise Willson, following the same idea, expose such elements as boron, silicon, magnesium, and titanium as are capable of combining with nitrogen at high temperatures, to the heat of an electric furnace in presence of carbon and nitrogen, using a current of high tension. Franck obtained aluminum nitride by heating the finely divided metal with powdered calcium carbide in a crucible and declares that when the metal is

heated with dry slaked lime the nitride may be obtained in large quantity. Practically all the nitrides yield ammonia when mixed with water. In the cold the aluminum compound decomposes but slowly, and Franck suggests that on this account it may have considerable manurial value. The production of nitrides in the electric furnace by the methods of Mehner and of Willson may become profitable sources of ammonia.

Experiment in the production of cyanides has been particularly active and practical advances have been made toward the acquirement of sources heretofore unavailable. In the old method of fusing nitrogenous organic matter with alkalies and iron, comparatively little improvement has been made. Bower adds iron thiocyanate to the melt toward the end of the operation and claims to secure thereby an increased yield. Reichard and Bueb submit lyes and molasses to dry distillation and slowly pass the gases generated through flues heated to  $1,000^{\circ}$  to  $1,100^{\circ}\text{C}$ . The gases finally pass through an absorber charged with a solution of iron salts. For such absorption Holmes recommends the use of an alkaline liquid in which ferrous carbonate is suspended. Drehschmidt recommends a mixture obtained by decomposition of a ferrous salt with calcium or magnesium carbonate and declares that this mixture is particularly favorable to the extraction of the cyanides from illuminating and coke-oven gases when much carbon dioxide and hydrogen sulphide are present. From the gas of coke-ovens the quantity of cyanides to be obtained is said to be variable according to the temperature of the oven. Thus a published report states that with a temperature of  $900^{\circ}\text{ C}$ . eight grams of sodium ferrocyanide was obtained from a cubic meter of gas, while with a temperature of  $950^{\circ}\text{ C}$ . the yield was increased to fifty-six to ninety-five grams of the salt.

Aitken proposes special construction and operation of blast furnaces with a view to the production and recovery of cyanogen. Two stacks erected alongside each other and rather higher than usual are connected by a lateral tube or pipe at the top. When the blast has been shut off from one and the slag and metal are being drawn off, a draft is started through an opening near the tuyeres and gases from the second furnace, drawn downward through the heated charge of the first. When the charge has finally been drawn off, the draft is stopped and the blast started again. When the second furnace is being tapped, the draft is made from a similar opening near the tuyeres and gases from the first furnace drawn downward through the charge of the second. In this way the furnaces are operated alternately and the gases drawn off are said to be particularly rich in cyanogen.

Nikodem Caro, in *Die Chemische Industrie*, and Conroy, in a paper presented to the Society of Chemical Industry, of England, have discussed the production of cyanides in a most interesting and instructive manner, the former from a more or less theoretical standpoint and the second from the results of a series of critical experiments made for the United Alkali Company. Both of these papers are full of practical suggestion and well worth careful study by every one interested in this branch of chemical industry. Naturally, both these authorities classify the methods used and available, as follows: (1) those producing cyanides directly and involving the use of atmospheric or other nitrogen and heat, and (2) wet methods with intermediate production of the thiocyanates. Neither, however, recognize the methods involving the reduction of oxidized nitrogen compounds. Under the first class Caro discusses the history of the reaction, and the work of Liebig, Karmrodt, Beilby, Barr and MacFarland, Siepermann, and others, in which, in various ways ammonia gas is brought into contact with carbon, impregnated with potash. Karmrodt obtained a yield of only about twenty per cent. of the theoretical. Beilby hoped to improve upon it by adding to the carbon-alkali mixture twenty per cent. of potassium cyanide, whereby it could be kept fluid, allowing the mass to flow over gratings arranged in a vertical column, while the ammonia gas was passed upward through the same column. Barr and MacFarland considered cyanide to be formed by double decomposition of carbon monoxide and ammonia, and Siepermann proved that the reaction between potassium carbonate and ammonia was possible without the intervention of carbon forming cyanate, potash, and water. To avoid the subsequent reduction of the cyanate with carbon he proposed mixing the potassium carbonate with barium carbonate and carbon, making a single operation of the reactions, and Caro declares that experience with the process shows it to be perfectly operative.

Conroy, discussing these reactions from the standpoint of his own experiments, states that operating with the process of Grüneberg, absorbing the ammonia at a low temperature and reducing the resulting cyanate at a higher temperature with carbon, he obtained a yield of only four per cent. of the ammonia entering the apparatus. With the process of Young and MacFarland, heating in a bent tube to 1,000° to 1,200°C. caustic potash and carbon in the proportion of 10:1 by weight, adding powdered charcoal from time to time till the weight added reached twenty to thirty per cent. of the weight of the potash used, he passed through the molten mass a carefully dried mixture of nitrogen, carbon monoxide, and ammonia, and secured a conversion to cyanide of thirty to thirty-three per cent. of the ammonia used. Time seemed to be an important element in the

reaction and production seemed to increase with the proportion of cyanide present.

Caro, discussing the methods involving the use of free nitrogen and heat, offers an extended review of the history of the reaction and process depending upon it from its discovery by Bunsen and Playfair to the present, and accepts Berthelot's explanation of the reaction that it depends upon the formation of potassium carbide, which in the heated condition may combine with nitrogen to form potassium cyanide. This, he considers, would satisfy the conditions of the process of Lambilly which, he says, consists in heating a mixture of potassium, sodium or barium carbonates with carbon as long as carbon monoxide is evolved and passing over the resulting mass at white heat, equal parts of nitrogen and illuminating gas, under pressure corresponding with ten to fifteen cm. of mercury. But Lambilly subsequently modified his process by first producing pure acetylene and passing this in admixture with pure atmospheric nitrogen over the hot alkali and carbon. Again, in the application of the Fogarty process in Pittsburg, whereby a mixture of finely divided lime and coke were fed into the top of a narrow vertical furnace provided with baffling plates and heated from the top to a temperature of 2,200° F. by the products of the imperfect combustion of a natural gas, cyanides were produced under conditions favoring the production of acetylene and its subsequent contact with heated alkali and carbon. A question naturally arises as to the possible part of acetylene in this reaction.

Both Caro and Conroy seem to consider the wet method of Gelis and its modifications to be the most promising. This, it will be remembered, consists in heating together ammonia and carbon disulphide, converting the ammonium thiocyanate into the corresponding calcium salt and this, in turn, by means of potassium sulphate into the potassium salt, which may then be desulphurized with iron. The process is said to be carried out by Grolich and Wichmann, in Hamburg, but the desulphurization by iron is found to be satisfactory only when filings are used in double the theoretical quantity and the whole heated under pressure to 110° to 120° C., whereby 80 per cent. of the theoretical yield is obtained.

Conroy, like others, found the consumption of ammonia, due to the production of sulphide, to be inconveniently high, and the pressure resulting from the production of hydrogen sulphide to be troublesome. He favors the suggestion of Hood and Salomon that manganese dioxide alone, or mixed with lime, be added to the charge, whereby their cyanides and sulphides are produced, leaving all the ammonia available for conversion into cyanide. Operating under the suggestions of Crowther and Ros-

siter, and of Hurter and Hethrington, Conroy heated together in a properly constructed jacketed vessel slaked lime, water, ammonia, and carbon disulphide, agitating the mixture and keeping it at a temperature of  $100^{\circ}\text{C}$ . for two hours. The thiocyanate remains in solution after distilling off the excess of ammonia and precipitating the lime with carbon dioxide. Conroy obtained quantitative results with this method.

From the results of his experiments he concludes:

1. "That the reaction between carbon disulphide and ammonia to form thiocyanate proceeds easily and completely. The addition of lime does not influence the yield one way or another, provided ammonia is present in excess, but simply serves to reduce the pressure within the apparatus.

2. "That carbon disulphide and calcium sulphide combine quantitatively in theoretical quantities when treated under suitable conditions to form soluble thiocarbonate. The combination takes place in the cold or at  $100^{\circ}\text{C}$ ., but especially well at  $50^{\circ}$  to  $60^{\circ}\text{C}$ .

3. "That the solution of calcium thiocarbonate may be quantitatively converted under suitable conditions into thiocyanate. For good yield, large excess of ammonia must be present."

It has been proposed to replace part of the lime by magnesia, which under pressure absorbs hydrogen sulphide, evolving the gas below  $100^{\circ}\text{C}$ ., or release of the pressure, while the base is precipitated for reuse.

For desulphurization of the thiocyanate Conroy favors the use of iron. To secure a good reaction (1) the material must be perfectly dry, (2) the iron must be finely divided, (3) the substance must be intimately mixed, and (4) a reducing atmosphere must surround the reacting mass.

Since the publication of these papers of Caro and Conroy, many interesting developments in the production of cyanides have been made, modifying or extending the old processes or introducing new ones. Troyman passes the gases issuing from the Bessemer converter between the cooling period and the drop of the flame into a basic-lined chamber filled with coke saturated with alkali carbonate, and recovers the cyanide by subsequently leaching the coke. Swan and Kendal mix carbon and tungsten, or saturate charcoal with potassium tungstate, heat the mixture in a properly protected tube of nickel or iron, cause a current of fused potassium carbonate to flow through the tube along with free nitrogen or ammonia, collecting the resulting cyanide in a suitable receiver at the lower end of the tube. Rad and Rosenfels heat such carbides as barium and calcium in a current of nitrogen or ammonia gas and get better results when the carbides are mixed with alkali carbonates. When ammonia is

used, hydrogen is liberated. Caro and Frank find that cyanogen compounds are formed when nitrogen and aqueous vapor are passed over carbides heated to dark redness in closed vessels. In practice they charge finely divided barium carbide into a tube-shaped retort, provided with inlet and outlet for gases and vapors. Nitrogen gas saturated with moisture is passed through the retort, and at the end of two hours the reaction is complete and the charge is withdrawn. They subsequently modified their process by passing ammonia gas over the heated carbides, forming alkaline cyanide and free hydrogen.

Pflege has made the interesting discovery that the absolute exclusion of oxygen is not necessary to cyanide formation. He uses a flat, covered, magnesia-lined furnace, whose sole is covered with a mixture of carbon and alkali in thin layer, and through which air may freely circulate. The space in the furnace above the charge and under the cover is proportioned to the quantity of air needed for local combustion. The furnace is so heated from below that the carbon may become ignited in contact with air, and during the resulting combustion cyanide production is said to proceed rapidly and with very high yield. The reaction is completed at the end of three hours. He modifies his process by placing 1,000 parts of potash and 100 parts of carbon in a crucible and heating the mass to 900° C., producing fusion. Then through a tube passing through the cover and projecting into the mass, he introduces a rapid stream of ammonia. As the carbon is consumed an additional quantity is blown in with the ammonia. At the end of three hours the alkali should all be converted into pure cyanide without by-products or impurities.

Bergmann, by passing a mixture of ammonia and coal-gas over carbon heated to 1,180° C., obtained conversion of sixty per cent. of the ammonia to cyanogen. One-half the residual ammonia was recovered and the remainder split up. Exclusion of oxygen seemed favorable to the reaction.

With all the manifold uses of the electric furnace it is natural that it should be applied to the production of the cyanides. Willson heats a metal or metalloid together with carbon in the electric furnace and subjects the heated mass to a current of nitrogen or producer gas, forming nitrides and cyanides, or the gases are passed through heated carbides in a separate furnace. Readman heats the oxides or carbonates of the alkali metals together with iron and carbon in an upright furnace with an electrode at the top and bottom and passes nitrogen or generator gases over the incandescent mass, collecting the fused cyanide or ferrocyanide at the bottom. Horning generates metallic vapors in the electric furnace and mixes them with carbon or

carbon compounds, preferably hydrocarbon gas or vapor and nitrogen, using considerable excess of the carbon and nitrogen. Mehner charges a U-shaped furnace with carbon and a fusible cyanide such as the barium compound and electrolyzes the mass, liberating cyanogen gas at the positive pole and barium at the negative pole. Generator gas is passed through the mass during the operation, the nitrogen combining with the carbon to form cyanogen which in turn combines with barium and is ultimately liberated at the anode. Blackmore prepares iron carbide in the electrical furnace, pulverizes the product, suspends it in a bath of fused alkali sulphide and passes nitrogen through the fused mass.

Castner makes use of the reaction between sodium and ammonia forming sodium amide and that between sodium amide and carbon producing the cyanide. His process is carried out in two operations in different apparatus. Sodium is fused and charged to a properly constructed retort from which air is excluded and heated to 300° to 400° C. Thoroughly dried ammonia gas is passed into the retort and the amide formed is conveyed to a second vertical retort which is charged with carbon and heated to dark redness. The amide dropping upon the carbon is converted into cyanide with the liberation of hydrogen and the resulting cyanide is drawn off from the bottom of the retort in a fused condition.

Moise utilizes boron nitride formed by heating borax in vapor of ammonium chloride for the production of cyanide. The compound mixed with carbon and potassium carbonate is heated to red heat in a crucible for about an hour. The resulting mass, consisting of potassium borate and potassium cyanide, is leached with alcohol dissolving the cyanide, leaving the borate for reuse.

Finlay mixes equal parts of carbon and alkali or alkaline earth (preferably barium carbonate), heats the mixture in a retort to 1,000° C., and subjects it at this temperature to a current of nitrogen and sulphur dioxide gases. When sufficient barium cyanide has been formed, the mass is pulverized, the barium cyanide and thiocyanate leached out, the leach decomposed with carbon dioxide and the cyanogen liberated collected in a soda solution. The barium carbonate is used in a succeeding charge.

Kerp has observed that when sodium acetate and sodium nitrite are fused together sodium cyanide is produced and that though in his experiment decided quantities of cyanogen gas escaped, the amount obtained was more than twenty-five per cent. of the theoretical yield.

Kellner found that when a nitrate or nitrite is subjected, either alone or mixed with nitrogen-free carbon, to the action of an arc between carbon electrodes of an electric furnace, cyanides

are produced, and Huntington has patented a process in which a mixture of acetylene and nitrous oxide in about equal volumes are drawn into the cylinder of a gas engine and exploded with a spark. The products of the explosion consisting of carbon monoxide, hydrogen, and cyanogen are passed through an alkaline solution whereby the cyanogen is absorbed and the other gases are allowed to pass along to be used as fuel.

Hood and Salomon produce thiocyanates by heating together caustic soda, carbon disulphide and ammonia, and desulphurize the resulting compound with lead or zinc. They find further that for the production of cyanogen compounds carbon disulphide may be replaced by carbon dioxide. In utilizing this principle, which seems opposed to past experience in this branch of chemical industry, they mix alkaline carbonate with finely divided zinc or manganese, heat the mass in a retort provided with a stirring gear and pass over the heated mass a current of ammonia gas. If sodium carbonate and zinc are used the products of the reaction are sodium cyanide, sodium hydroxide, zinc oxide, and water. It is recommended that a small quantity of carbon be added to the mixture to increase the yield of cyanide. The zinc oxide is reduced and enters again into the reaction.

Goerlich and Wichmann heat together in an autoclave provided with a stirring gear, a mixture of sodium nitrite, carbon disulphide, and hydrogen sulphide for the production of thiocyanate. The temperature is maintained at 150° C. and the operation continued until the manometer indicates a lowering of the pressure and therefore the end of the reaction.

According to Raschen and Brock, desulphurization of thiocyanate may be effected by treating it with nitric acid with exclusion of air. If sodium thiocyanate for instance is allowed to flow into dilute nitric acid, hydrocyanic acid and nitric oxide are liberated. The gases are passed through a scrubber with water at 80° C. to retain the nitrous vapors and the hydrocyanic acid passing along is collected in cold water or an alkaline solution. Nitric acid is regenerated from the oxide for reuse.

Lutke secures desulphurization of the thiocyanates by mixing ninety-seven parts of the potassium compound with sixty-five parts of zinc dust and heating the mass in an iron crucible with stirring. When the mass glows the external heat is withdrawn and the reaction allowed to progress. The reaction applied in this way is stated to furnish ninety per cent. of the theoretical yield.

Bower first converts the soluble thiocyanate into the copper salt by double decomposition with cuprous chloride. The copper compound is suspended in an autoclave with finely divided

iron and heated under pressure. Copper sulphide and ferrous cyanide result and the latter is treated with an alkali to produce soluble ferrocyanide.

Tschermak mixes thiocyanate with ninety per cent. of its weight of dried oxide of iron and heats the mixture at 450° C. for one hour. The resulting mass contains an amount of cyanate corresponding with 90 per cent. of the theoretical yield, together with a little alkaline sulphate. The cyanate is purified by recrystallization at 0° C. when the sulphate separates.

To prevent the production of cyanates in the treatment of ferrocyanide for cyanide, Chaster grinds together the anhydrous ferrocyanide and alkaline carbonate in proper proportions and mixes the mass with finely divided wood-charcoal, or with gas-tar, resin, bitumen or similar substances, after which it may be treated in the furnace in the usual way.

In the reactions and processes here set forth, even though they may not all be operative and though some may even be questionable, there is food for fruitful study and much help for future work. And they illustrate the promptness with which rational investigation responds to the commercial demand.

Wm. McMURTRIE.

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#### OBITUARY.

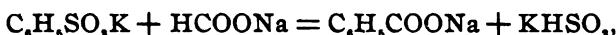
VICTOR MEYER, who died on the 8th of August, was born in Berlin on the 8th of September, 1848. His first published chemical investigation appeared in April, 1869, and was published from the laboratory of Professor Baeyer, who was at that time professor of chemistry at the Gewerbe Academie in Berlin.

In 1871 Meyer was made professor of chemistry at Stuttgart; in 1872 he was called to Zurich; in 1885 he went as professor of chemistry to the University of Göttingen, where he remained until 1889, when, upon the retirement of Professor Bunsen, Meyer was called to his place as professor of chemistry in the University of Heidelberg.

Meyer was an extremely active and able chemical investigator. His activity is shown by the fact that since the appearance of his first paper in 1869 there have appeared in the *Berichte der deutschen chemischen Gesellschaft*, up to the time of his death, 275 separate papers from his pen, with hosts of other papers from his laboratory, the work of which was suggested and inspired by him. Besides the papers published in the *Berichte*, occasional

papers have appeared in Liebig's *Annalen*, the *Journal für praktische Chemie*, the *Zeitschrift für physikalische Chemie*, and the *Zeitschrift für anorganische Chemie*; added to these are lectures and addresses published in the more popular journals. While the large number of his published papers testifies to his activity, their intrinsic worth and the unusual number of really important papers among them gives ample evidence of his great ability.

One of his early investigations gave to organic chemistry the reaction



which is now frequently made use of to introduce the carboxyl group into aromatic compounds. Meyer was the first to prepare a nitro-paraffin, and practically all that is known about this interesting group of compounds is due to Meyer and his pupils. His work upon the ammonium bases and his discussion with Ladenberg over the points raised, a discussion which unfortunately mingled with considerable personal feeling on the part of these two experimenters, is familiar to most students of organic chemistry.

In 1883 Meyer announced his discovery of thiophene in commercial coal-tar benzene, which in spite of its large contents of sulphur, had been previously overlooked on account of the close resemblance of its properties to the properties of benzene. Following this came a long series of articles by Meyer and his pupils, giving full accounts of thiophene and its derivatives.

In 1882 Meyer and Janny made clear the structure of the oximes, and in the following year Meyer and Goldschmidt, in studying the action of hydroxylamines on benzil, obtained two isomeric benzil dioximes. A careful study of these compounds forced them to the conclusion that they both had the same structural formula. In 1888 Meyer and Auwers attempted to explain this isomerism by considerations based upon the stereochemistry of carbon. Van't Hoff and Wislicenus have assumed that when carbon atoms are singly linked there is free rotation around their common axis. They pointed out that unless this free rotation was assumed isomeric modifications would result. Meyer and Auwers suggested that the evidence of the two iso-

meric benzil dioximes could be explained if free rotation in their case were not assumed. It is necessary, according to this view, to assume two different kinds of single union between two carbon atoms, one which permits of free rotation, and one which does not.

Later in the same year Meyer and Reicke put forward an ingenious hypothesis concerning the nature of valence in the carbon atom in order to explain the lack of free rotation in some cases of singly linked carbon atoms. These views have never strongly appealed to chemists. One probable reason for this being that the speculations of Meyer and Reicke were followed very closely by a paper from Hantzsch and Werner upon the stereochemistry of nitrogen, in which the isomerism of the oximes was referred to the nitrogen atoms in a manner that gave a simpler, and on the whole, more satisfactory explanation of the subject.

Stereochemistry (a name which by the way was first suggested by Meyer), has been a favorite field of investigation for Meyer, and he has made many contributions, both experimental and theoretical, to the rapid advance of this subject.

In 1894 Meyer introduced to the chemical world a new series of organic bases which contained iodine but no nitrogen, which he called iodonium bases.

Meyer's work has not been limited to the field of organic chemistry. His apparatus for the determination of the vapor-density of liquids and solids is perhaps in more common use than any other.

By using platinum and porcelain vessels he has studied the vapor-density of numerous inorganic compounds and elements at a white heat. In this connection I cannot do better than quote from an address made by Meyer, at Heidelberg, in 1889: "To-day new methods of experiment permit of comparatively easy determination of the vapor-density and consequently of the molecular state of substance at the highest temperatures. Numerous inorganic compounds, and the elements themselves, have been studied with regard to their vapor density at a white heat. While many of them, as oxygen, nitrogen, sulphur, and mercury, remain unchanged under such conditions, the molecules

of chlorine, bromine; and iodine were split into two atoms in conformity with Avogadro's surmise in regard to the compound nature of the elementary molecules. In the same manner the vapor-density and the molecular condition of the less volatile elements, zinc, thallium, antimony, and bismuth were successfully determined at a white heat. To-day pyrochemical work is limited to a temperature of 1,700° C., because vessels of porcelain and platinum, to the use of which we are limited, fuse above that temperature.

"The possibility of performing quantitative experiments at those temperatures seemed to us, some few years ago, to be an unexpected progress, but to-day we complain that the trivial cause of a want of proper vessels forbids us to increase the temperature to 2,000° or 3,000° C. There is no doubt that we should arrive at new unthought-of facts, that the splitting of other elementary molecules would be possible, that a new chemistry would be revealed to us, if, being provided with vessels of infusible material, we could work at temperatures at which water could not exist, and at which detonating gas would be a non-inflammable mixture."

In 1885 Meyer published a monograph upon his pyrochemical investigations. In 1888 he published another monograph upon thiophene and its derivatives. At the time of his death he was engaged with his colleague, Professor Paul Jacobson, in the preparation of a manual of organic chemistry, the second volume of which approaches completion. This work, so far as published, is the best extended treatment of the subject known to the writer.

The death of Victor Meyer in the midst of his work and in the prime of life is an irreparable loss to chemistry—it is a loss that will be much lamented wherever chemistry is studied.

G. M. RICHARDSON.

SEPTEMBER 21, 1897.

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#### BOOKS RECEIVED.

**Electric Smelting and Refining. The Extraction and Treatment of Metals by Means of the Electric Current.** Being the second edition of "Elektro-Metallurgie." By Dr. W. Borchers. Translated, with additions, by Walter G. McMillan: London: Charles Griffin & Co., Limited;

Philadelphia: J. B. Lippincott Company. 1897. xx + 416 pp. Price, \$6.50.

Cider Vinegar of Pennsylvania. By Dr. William Frear. Bulletin No. 22, Pennsylvania Department of Agriculture. Harrisburg, Pa. 27 pp.

Verzeichniss sämmtlicher Präparate, Drogen und Mineralein mit Erläuterungen. E. Merck, Darmstadt. 1897. vi + 306 pp.

Soil Moisture: A Record of the Amount of Water contained in Soils during the Crop Season of 1896. By Milton Whitney and Ralph S. Hosmer, U. S. Department of Agriculture, Division of Soils. Washington: Government Printing Office. 1897. 23 pp.

Monthly List of Publications of the U. S. Department of Agriculture, Division of Publications. Washington, D. C. September, 1897. 3 pp.

An Introductory Course in Quantitative Chemical Analysis. By Percy Norton Evans, Ph.D., Associate Professor of Chemistry in Purdue University, Lafayette, Indiana. Boston: Ginn & Company. 1897. pp. iv + 83. Price, 55 cents.

The Principles of Chemistry. By D. Mendeléeff. Translated from the Russian (Sixth Edition) by George Kamensky, A. R. S. M. Edited by T. A. Lawson, B.Sc., Ph.D. Vol. I. xviii + 621 pp. Vol. II. i + 518 pp. 1897. New York: Longmans, Green & Co. Price, 2 vols., \$10.00.

Manual of Qualitative Chemical Analysis. By the late Dr. C. Remigius Fresenius. Authorized translation by Horace L. Wells, M.A. New Edition, Thoroughly Revised, from the Sixteenth German Edition. xvii + 748 pp. 1897. New York: John Wiley & Sons. Price, \$5.00.

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## THE JOURNAL

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# AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF CINCINNATI.]

### LVI.—SALTS OF DINITRO- $\alpha$ -NAPHTHOL WITH VARIOUS METALLIC BASES.

BY T. H. NORTON AND H. LOEWENSTEIN.

Received January 18, 1897.

THE preparation and study of the following compounds were undertaken with the view of ascertaining whether in addition to the few salts of dinitro- $\alpha$ -naphthol thus far known, there might not be other combinations with metallic bases possessing a greater degree of solubility than the commercial calcium salt (Manchester yellow, Martius Gelb) now so largely used, or more especially showing distinct variations in the color imparted to animal and vegetable fibers. The results showed that in the latter respect the metal present is practically without influence on the tinctorial properties of dinitro- $\alpha$ -naphthol, the tint yielded in each individual case being essentially that imparted by the free phenol or by its calcium salt.

The salts of dinitro- $\alpha$ -naphthol thus far examined and analyzed are those with sodium,<sup>1</sup> potassium,<sup>1</sup> ammonium,<sup>2</sup> barium,<sup>2</sup> strontium,<sup>2</sup> calcium,<sup>3</sup> and silver.<sup>1</sup>

The dinitro- $\alpha$ -naphthol used was prepared by precipitating

<sup>1</sup> Hübner: *Ann. Chem. (Liebig)*, 208, 332.

<sup>2</sup> Martius: *J. prakt. Chem.*, 102, 443.

<sup>3</sup> Darmstädter and Wichelhaus: *Ann. Chem. (Liebig)*, 157, 201; Liebermann: *Ann. Chem. (Liebig)*, 183, 249; Martius: *Vide supra*.

the concentrated aqueous solution of the commercial calcium salt by dilute sulphuric acid, washing the precipitate thoroughly with water, drying, and extracting the liberated phenol by boiling alcohol. The finely crystallized product thus obtained possessed the melting-point of 138°.

**LITHIUM DINITRO- $\alpha$ -NAPHTHOLATE,  $C_{10}H_8(NO_2)_2OLi$ .**

This salt is obtained in solution by boiling an excess of dinitro- $\alpha$ -naphthol with an aqueous solution of lithium carbonate and filtering. On evaporation it is deposited in the form of a brilliant crimson powder, which is amorphous and anhydrous. The salt, on being heated to 295°, explodes before melting. It is soluble in ninety-six parts of water at 19°, in fourteen parts of boiling water, in fifty parts of cold alcohol, in fifteen parts of boiling alcohol, and in 300 parts of ether. It is insoluble in carbon disulphide and in benzene. The temperature of solutions, unless otherwise noted, is 18° C.

The salt, dried between sheets of bibulous paper, lost no weight on heating to 105°. The analyses were made by adding concentrated sulphuric acid to weighed amounts in a platinum crucible, evaporating to dryness and ignition as lithium sulphate. Care is necessary to avoid spattering.

I. 0.246 gram of the dry salt gave 0.0535 gram lithium sulphate, equal to 0.0069 gram of lithium, or 2.80 per cent.

II. 0.256 gram gave 0.0535 gram lithium sulphate, equal to 0.0068 gram of lithium, or 2.88 per cent.

|               | Calculated for<br>$C_{10}H_8N_2O_4Li$ . | Found.         |
|---------------|---|----------------|
|               | I.                                      | II.            |
| Lithium ..... | 2.87                                    | 2.80      2.88 |

**MAGNESIUM DINITRO- $\alpha$ -NAPHTHOLATE,  $[C_{10}H_8(NO_2)_2O]_2Mg$ .**

This salt is prepared by boiling in water a mixture of magnesium carbonate with an excess of the naphthol. It crystallizes slowly from the filtered solution in the form of reddish needles, grouped in rosettes. It is anhydrous, the salt dried between sheets of bibulous paper, losing no weight when heated to 105°. It is soluble in 792 parts of water at 20°, in 154 parts of boiling water, in 436 parts of cold alcohol, in 144 parts of boiling alcohol, and in 260 parts of ether. It is insoluble in benzene and carbon disulphide.

The first three analyses were made by igniting the substance in a platinum crucible, in which a smaller inverted crucible was wedged so as to prevent as much as possible mechanical loss by explosive decomposition, and weighed as magnesia.

In the fourth analysis the substance was strongly heated in a sealed tube. After cooling, the tube was opened, its contents were dissolved in dilute nitric acid, and the solution was evaporated to dryness, ignited, and weighed likewise as magnesia.

I. 0.035 gram of the salt dried at 105° gave 0.0025 gram magnesium oxide, equal to 0.0015 gram magnesium, or 4.28 per cent.

II. 0.1557 gram gave 0.0113 gram magnesium oxide, equal to 0.067 gram magnesium, or 4.35 per cent.

III. 0.1552 gram gave 0.012 gram magnesium oxide, equal to 0.0072 gram magnesium, or 4.64 per cent.

IV. 0.0623 gram gave 0.0039 gram magnesium oxide, equal to 0.0023 gram magnesium, or 3.77 per cent.

|                | Calculated for<br>$(C_{10}H_8N_2O_4)_2Mg.$ | I.   | II.  | Found.<br>III. | IV.  |
|----------------|--|------|------|----------------|------|
| Magnesium..... | 4.87                                       | 4.28 | 4.35 | 4.64           | 4.77 |

#### ZINC DINITRO- $\alpha$ -NAPHTHOLATE, $[C_{10}H_8(NO_2)_2O]Zn$ .

This is obtained by boiling together in water an excess of the naphthol with zinc carbonate. From a hot concentrated solution it crystallizes out in the form of handsome reddish-yellow needles, while more dilute solutions yield reddish crystals, possessing the shape of rhomboidal plates. In this respect the zinc salt resembles the calcium salt.<sup>1</sup>

It is soluble in 960 parts of water at 20°, in 300 parts of boiling water, in 250 parts of cold alcohol, in 115 parts of boiling alcohol, and in 150 parts of ether. It is insoluble in benzene and carbon disulphide. The salt is anhydrous, crystals dried between sheets of bibulous paper losing no weight at 105°.

The explosive nature of the compound renders necessary in analysis the careful use of the two crucibles described above, small amounts being taken. Even with these precautions a small loss is unavoidable.

I. 0.123 gram of the salt dried at 105° gave 0.017 gram zinc oxide, equal to 0.0136 gram zinc, or 11.09 per cent.

<sup>1</sup> Liebermann: *Ann. Chem. (Liebig)*, 183, 249.

II. 0.108 gram gave 0.016 gram zinc oxide, equal to 0.0128 gram zinc, or 11.89 per cent.

|            | Calculated for<br>(C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> Zn. | Found.           |
|------------|--|------------------|
|            | I.   | II.              |
| Zinc ..... | 12.22  | 11.09      11.89 |

COPPER DINITRO- $\alpha$ -NAPHTHOLATE, [C<sub>10</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>O]Cu.

This salt is obtained by adding an excess of a concentrated solution of copper chloride to a cold aqueous solution of ammonium dinitro- $\alpha$ -naphthol. The chocolate-colored precipitate is washed with water until all traces of copper chloride are removed, and dried between sheets of bibulous paper. Thus prepared, it is an anhydrous, dark-brown, amorphous powder, the most insoluble of the salts of the naphthol thus far known.

It dissolves in 5.750 parts of water at 21°, in 2.165 parts of boiling water, in 1.007 parts of cold alcohol, in 954 parts of boiling alcohol, and in 2.615 parts of ether. It is insoluble in benzene and carbon disulphide.

The analyses were performed by gently heating the salt with concentrated nitric acid in a covered porcelain crucible, and finally igniting. As in the preceding cases, the explosive nature of the salt renders the utmost care necessary.

I. 0.2663 gram of the salt dried at 105° gave 0.036 gram cupric oxide, equal to 0.0287 gram copper, or 10.79 per cent.

II. 0.1665 gram gave 0.023 gram cupric oxide, equal to 0.0183 gram copper, or 11.03 per cent.

III. 0.3033 gram gave 0.0443 gram cupric oxide, equal to 0.0353 gram copper, or 11.67 per cent.

|             | Calculated for<br>(C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> Cu. | Found.           |       |
|-------------|--|------------------|-------|
|             | I.   | II.              | III.  |
| Copper..... | 11.97  | 10.79      11.03 | 11.67 |

SOLUBILITIES OF THE AMMONIUM AND CALCIUM SALTS.

No data existing on the solubilities of these two compounds, the following determinations were made :

Ammonium dinitro- $\alpha$ -naphtholate is soluble in 600 parts of water at 25°, in thirty-eight parts of boiling water, in 113 parts of cold alcohol, in 57 parts of boiling alcohol, and in 1,124 parts of ether.

Anhydrous calcium dinitro- $\alpha$ -naphtholate is soluble in 1,656

parts of water at 20°, in eighty-six parts of boiling water, in forty-seven parts of cold alcohol, in fifteen parts of hot alcohol, and in forty-five parts of ether.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

## LVII. ON CERTAIN AMINE DERIVATIVES OF DINITRO- $\alpha$ -NAPHTHOL AND ITS CHLORINATION.

BY T. H. NORTON AND IRWIN J. SMITH.

Received January 18, 1897.

In connection with a recent study of dinitro- $\alpha$ -naphthol derivatives,<sup>1</sup> the following salt of this phenol with various amines were prepared and analyzed. The dinitro- $\alpha$ -naphthol used was prepared from the commercial calcium salt by treatment with sulphuric acid and recrystallization from alcohol. It possessed the correct melting-point of 138°.<sup>2</sup>

TRIMETHYLAMINE-DINITRO- $\alpha$ -NAPHTHOLATE,  
 $C_{10}H_8(NO_2)_2OH.N(CH_3)_3$ .

This salt was prepared by boiling dinitro- $\alpha$ -naphthol with an excess of a thirty-three per cent. aqueous solution of trimethylamine. The product was crystallized from alcohol and obtained in the form of long, lustrous, red needles, which are anhydrous and melt at 190° (uncorr.). The salt is soluble in 909 parts of water at 18°, in fifteen parts at 100°, in 200 parts of cold alcohol, in 40 parts of boiling alcohol, and in 4,000 parts of ether. It is insoluble in carbon disulphide and in benzene. The temperature of solutions in all cases, when not otherwise noted, is 18° C.

Analysis: 0.2154 gram of the salt dried at 100° gave 0.0969 gram water or five per cent. of hydrogen, and 0.4193 gram carbon dioxide or 53.06 per cent. of carbon.

|                | Theory. | Found. |
|----------------|---------|--------|
| Carbon .....   | 53.24   | 53.06  |
| Hydrogen ..... | 5.12    | 5.00   |

The yellow solutions of the salt resemble in tinctorial power those of dinitro- $\alpha$ -naphthol itself.

<sup>1</sup> Norton and Loewenstein: This Journal, 19, 923.

<sup>2</sup> Martius: *Ztschr. Chem.*, 1868, 80.

**ANILINE-DINITRO- $\alpha$ -NAPHTHOLATE,**  
**C<sub>10</sub>H<sub>8</sub>(NO<sub>2</sub>)<sub>2</sub>OH.NH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>**.

This salt was prepared by boiling together in molecular proportions, aniline and dinitro- $\alpha$ -naphthol in alcoholic solution. The resultant solution was allowed to crystallize by spontaneous evaporation, and the crude product was recrystallized from alcohol three times before a constant melting-point was attained. The salt thus prepared is obtained in the form of light yellow, fine, acicular crystals united in rosettes, which melt at 129°. It is naturally anhydrous. It dissolves in 72,000 parts of water, in 264 parts of boiling water, in 200 parts of cold alcohol, in 130 parts of boiling alcohol, in 100 parts of ether, in 814 parts of carbon disulphide, and in 16,600 parts of benzene. The solutions are of a yellow color, and dye strongly.

Analysis: The salt lost no weight on heating to 100°. 0.0855 gram of the salt dried at 100°, gave 0.0285 gram of water or 3.71 per cent. of hydrogen, and 0.168 gram of carbon dioxide, or 53.59 per cent. of carbon.

|                | Theory. | Found. |
|----------------|---------|--------|
| Carbon .....   | 53.80   | 53.59  |
| Hydrogen ..... | 3.62    | 3.71   |

**ORTHOTOLUIDINE-DINITRO- $\alpha$ -NAPHTHOLATE,**  
**C<sub>10</sub>H<sub>8</sub>(NO<sub>2</sub>)<sub>2</sub>OH.NH<sub>2</sub>.C<sub>6</sub>H<sub>4</sub>.CH<sub>3</sub>**.

The preparation is similar to that of the aniline salt. It crystallizes in fine, silky, yellow needles, usually united in rosettes, which are anhydrous and melt at 132°. It is soluble in 6,800 parts of water, in 614 parts of boiling water, in fifty-two parts of cold alcohol, in seven and a half parts of boiling alcohol, in 60 parts of ether, and in 288 parts of carbon disulphide. It is insoluble in benzene. The tinctorial properties are similar to those of the aniline salt.

Analysis: 0.1635 gram of the salt dried at 100° gave 0.072 gram of water or 4.80 per cent. of hydrogen, and 0.3624 gram of carbon dioxide or 60.42 per cent. of carbon.

|                | Theory. | Found. |
|----------------|---------|--------|
| Carbon .....   | 59.82   | 60.42  |
| Hydrogen ..... | 4.40    | 4.80   |

DIMETHYL-ANILINE-DINITRO- $\alpha$ -NAPHTHOLATE,  
 $C_{10}H_8(NO_2)_2OH.N(CH_3)_2C_6H_5.$

The preparation is similar to that of the aniline salt above. It is obtained in the form of lustrous, large, thin, flat crystals of a yellowish-brown color, which are anhydrous and melt at 115°. It dissolves in 8,580 parts of water at 20°, in 455 parts of boiling water, in 255 parts of cold alcohol, in ten parts of hot alcohol, in 67.5 parts of ether, and in ninety parts of carbon disulphide. It is insoluble in benzene. The tinctorial properties are similar to those of the aniline salt.

Analysis: 0.0325 gram of the salt dried at 100° gave 0.7281 gram carbon dioxide or 61.07 per cent. carbon, and 0.0143 gram water or 4.89 per cent. hydrogen.

|                | Theory. | Found. |
|----------------|---------|--------|
| Carbon .....   | 60.86   | 61.07  |
| Hydrogen ..... | 4.78    | 4.89   |

NOTE ON THE CHLORINATION OF DINITRO- $\alpha$ -NAPHTHOL.

The following work was undertaken with the view of ascertaining whether the nitro group in aromatic compounds can be directly replaced by chlorine. Lellmann, in his *Principien der organischen Chemie*, states that there is no such case on record. The results of our experiments would tend to show that this substitution can take place, although they are not fully satisfactory.

Carefully purified dinitro- $\alpha$ -naphthol was placed in a U-tube immersed in a beaker of water, and was connected with a generator yielding dry chlorine. The temperature was maintained at 100°. The contents of the tube soon changed to a dull red, viscous mass, through which the gas bubbled. The color gradually deepened as chlorine was absorbed. The operation was continued for some days until there was no further increase in weight. 5.519 grams gained thus 0.364 gram in weight, or six and six-tenths per cent. The substance thus obtained was, when cold, of a dark yellow and viscous. It was slightly soluble in ether, alcohol, carbon disulphide, and benzene. From none of these solutions, however, could crystals be secured, nor could a distinct melting-point be obtained from any of the residues left on evaporation. A qualitative analysis showed the absence of nitrogen. A chlorine determination gave:

|                | Per cent. |
|----------------|-----------|
| Chlorine ..... | 21.77     |

Monochlor naphthol requires 19.66 per cent.; dichlor naphthol requires 33.02 per cent. There was evidently no simple substitution of Cl for NO<sub>2</sub>, and it was plain that more complicated changes than those involved by substitution had taken place. The inability to obtain a product offering the assurance of purity, caused a discontinuance of the work. The expulsion of the nitro group by chlorine under these conditions, is, however, worthy of note.

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### THE RATE OF SOLUTION OF SOLID SUBSTANCES IN THEIR OWN SOLUTIONS.

BY ARTHUR A. NOYES AND WILLIS R. WHITNEY.

Received October 11, 1897.

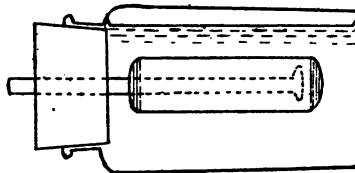
AS far as we know, the effect of the concentration on the rate at which a solid substance dissolves in its own solution, has not heretofore been investigated. This is probably due to the experimental difficulties in the way of keeping the surface of the dissolving substance constant during the solution.

The question is an important one, especially because of the light its solution would throw upon the attainment of the state of saturation, which is a matter of importance in all solubility determinations. Therefore we have investigated the phenomenon and have succeeded in experimentally establishing the law according to which the process takes place.

The experiments were carried out in the following manner: In order to keep the alteration of the surface-area of the dissolving substances as small as possible, the slightly soluble substances, benzoic acid and lead chloride, were chosen. Cylinders of these two substances, about eight cm. long and two in diameter, were prepared upon cores of glass. In the case of benzoic acid, this was done by simply pouring the melted acid into a test-tube containing a glass rod flattened a little at the lower end and protruding at the other end above the test-tube. When the whole had cooled, the cylinder of acid adhering well to the glass rod could usually be easily removed from the tube. It was found necessary in the case of lead chloride to proceed differ-

ently, because the cylinders of it, made as above, broke upon cooling. They were finally made by dipping the glass rods into the molten salt, removing then a second or two to allow them to cool, and repeating the operation until a sufficient amount had solidified upon the rods. Both ends of the cylinders of the two substances were coated with paraffin, and the free ends of the glass rods were forced through the centers of numbered paraffined corks, each of which fitted into a wide-mouthed bottle of 130 cc. capacity.

In conducting the experiments, exactly 100 cc. of distilled water were placed in each of the six bottles, and these were suspended in a thermostat kept at 25° C. within a few thousandths of a degree. After the temperature of the bath had been attained, the corks bearing the sticks of substance were inserted in the bottles so that the cylinders were in the middle of the bottle, and covered with water, as shown in the cut. The



time was then noted and the bottles were rotated<sup>1</sup> in a horizontal position in the bath exactly ten (or ten and a half) minutes, at the rate of sixty rotations per minute. The sticks were then removed from the bottles; and the solutions titrated directly, in the case of the benzoic acid, with sodium hydroxide solution, and in that of the lead chloride, with silver nitrate and potassium thiocyanate. The same sticks were then returned to the bottles, which were charged with new portions of 100 cc. of water, and were rotated as before for thirty, and finally for sixty minutes, when the resulting solutions were analyzed. In order to have as nearly as possible the same conditions in the different experiments, each series of three determinations was made with the same stick of material in the same bottle, and each series was repeated several times. During the time elapsing between separate rotations, the sticks were kept in saturated solutions of

<sup>1</sup> For a description of the rotation apparatus, see *Ztschr. phys. Chem.*, 9, 606.

the respective substances, so that they could not become dry, nor altered in surface.

The law governing the rate of solution can be predicted with a considerable degree of probability; for the phenomenon may be considered as simply a process of diffusion. That is, we can imagine the sticks of solid substances surrounded by an indefinitely thin film of saturated solution, from which diffusion takes place into all portions of the solvent, this being kept homogeneous by the rotation. If this were the case, the velocity of solution, in accordance with the law of diffusion, would be proportional to the difference between the concentration of the saturated solution and that of the solution present at the moment in question. This is then the law which is first to be tested. Its mathematical expression is:

$$\frac{dx}{dt} = C(S - x),$$

where  $S$  represents the solubility of the substance, or the concentration of its saturated solution;  $x$  the concentration at the expiration of the time  $t$ , and  $C$  a constant. Integration of the equation gives:

$$C = \frac{1}{t} \log_e \frac{S}{S - x}.$$

In order to obtain values for  $C$  in this equation, the solubility  $S$  of the substance must be known. This was determined in the usual manner<sup>1</sup> by rotating a large excess of the finely divided substance in the bottles of water, proceeding so that the condition of equilibrium was approached from both the undersaturated and supersaturated states. The results of the solubility determinations are given below. The separate values obtained are designated by  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$ , and the mean is represented by  $S$ . They are expressed in millimols per liter.

| Substance.         | $S_1$ . | $S_2$ . | $S_3$ . | $S_4$ . | $S$ . |
|--------------------|---------|---------|---------|---------|-------|
| Benzoic acid.....  | 27.88   | 28.11   | 27.96   | 27.75   | 27.92 |
| Lead chloride..... | 39.00   | 38.94   | 38.50   | 38.50   | 38.66 |

The results of the velocity experiments are given in the following table. The values of  $x_1$ ,  $x_2$ , etc., are the concentrations

<sup>1</sup> *Ztschr. phys. Chem.*, 16, 128.

in millimols of the solutions resulting from successive treatments, carried out as described above, of the same stick of substance. The values under  $x$  are the means of these single values.

## BENZOIC ACID.

## Stick No. 1.

| <i>t.</i> | $x_1.$ | $x_2.$ | $x_3.$ | $x_4.$ | $x_5.$ | $x_6.$ | $x.$  | $S-x.$ | <i>C.</i> |
|-----------|--------|--------|--------|--------|--------|--------|-------|--------|-----------|
| 10        | 6.27   | 6.69   | 6.55   | 6.77   | 6.20   | 5.62   | 6.35  | 21.57  | 112.1     |
| 30        | 14.45  | 14.47  | 15.22  | 15.27  | 14.48  | ....   | 14.78 | 13.14  | 109.1     |
| 60        | 21.70  | 21.44  | 22.56  | 21.80  | 20.51  | ....   | 21.60 | 6.32   | 107.5     |

## Stick No. 2.

|    |       |       |       |       |       |      |       |       |       |
|----|-------|-------|-------|-------|-------|------|-------|-------|-------|
| 10 | 6.32  | 6.40  | 6.33  | 7.64  | 6.43  | 5.16 | 6.38  | 21.54 | 112.7 |
| 30 | 15.33 | 15.19 | 15.50 | 16.39 | 15.12 | .... | 15.51 | 12.41 | 117.4 |
| 60 | 22.15 | 22.30 | 22.13 | 21.43 | 21.44 | .... | 21.89 | 6.03  | 110.9 |

## Stick No. 3.

|    |       |       |       |       |       |      |       |       |       |
|----|-------|-------|-------|-------|-------|------|-------|-------|-------|
| 10 | 8.84  | 9.32  | 9.07  | 9.22  | 8.15  | 7.85 | 8.74  | 19.18 | 163.0 |
| 30 | 18.15 | 20.15 | 19.73 | 17.63 | 16.81 | .... | 18.49 | 9.43  | 157.1 |
| 60 | 24.95 | 24.92 | 25.22 | 24.67 | 24.20 | .... | 24.79 | 3.13  | 160.1 |

## Stick No. 4.

|    |       |       |       |       |       |      |       |       |       |
|----|-------|-------|-------|-------|-------|------|-------|-------|-------|
| 10 | 5.47  | 5.52  | 6.49  | 6.28  | 5.77  | 5.72 | 5.87  | 22.05 | 102.5 |
| 30 | 14.05 | 14.36 | 14.21 | 14.97 | 13.40 | .... | 14.20 | 13.72 | 102.8 |
| 60 | 22.19 | ....  | 19.47 | 19.88 | 19.90 | .... | 20.33 | 7.59  | 94.3  |

## LEAD CHLORIDE.

## Stick No. 1.

| <i>t.</i>        | $x_1.$ | $x_2.$ | $x_3.$ | $x_4.$ | $x_5.$ | $x.$  | $S-x.$ | <i>C.</i> |
|------------------|--------|--------|--------|--------|--------|-------|--------|-----------|
| 10 $\frac{1}{2}$ | ....   | 5.96   | 6.56   | 5.70   | 6.35   | 6.14  | 32.52  | 71.5      |
| 30               | ....   | ....   | 15.9   | 15.5   | 15.8   | 15.73 | 22.93  | 75.6      |
| 60               | ....   | ....   | 25.5   | 35.7   | 22.5   | 24.58 | 14.08  | 72.7      |

## Stick No. 2.

|                  |      |      |       |      |       |       |       |       |
|------------------|------|------|-------|------|-------|-------|-------|-------|
| 10 $\frac{1}{2}$ | 9.93 | 9.01 | 10.05 | 9.40 | 10.21 | 9.73  | 28.93 | 119.0 |
| 30               | 23.8 | 20.6 | 22.6  | 22.7 | 22.2  | 22.38 | 16.28 | 125.4 |
| 60               | 31.9 | 31.9 | 30.4  | 31.9 | 30.8  | 31.38 | 7.28  | 120.9 |

## Stick No. 3.

|                  |      |      |      |      |      |       |       |      |
|------------------|------|------|------|------|------|-------|-------|------|
| 10 $\frac{1}{2}$ | 8.17 | 7.04 | 7.25 | 7.50 | 7.20 | 7.43  | 31.23 | 88.2 |
| 30               | 20.4 | 18.8 | 18.4 | 17.4 | 18.2 | 18.64 | 20.02 | 95.2 |
| 60               | 26.1 | 27.1 | 28.4 | 26.8 | 26.8 | 27.02 | 11.64 | 86.9 |

## Stick No. 4.

|                  |      |      |      |      |      |       |       |      |
|------------------|------|------|------|------|------|-------|-------|------|
| 10 $\frac{1}{2}$ | 6.18 | 4.84 | 4.81 | 4.17 | 4.50 | 4.90  | 33.76 | 56.0 |
| 30               | 15.1 | 15.4 | 13.7 | 12.0 | 11.4 | 13.52 | 25.14 | 62.3 |
| 60               | 23.1 | 23.0 | 22.6 | 21.2 | 18.0 | 21.58 | 17.08 | 59.2 |

It is evident from these results that the calculated constants vary usually irregularly and but little.

As this is the case with two substances of so widely different chemical nature and physical properties as benzoic acid and lead chloride, it is safe to assume that the law is a general one. It may be expressed as follows: The rate at which a solid substance dissolves in its own solution is proportional to the difference between the concentration of that solution and the concentration of the saturated solution.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MAY, 1897.

## THE ANALYSIS OF BEARING-METAL ALLOYS, WITH A NEW VOLUMETRIC METHOD FOR DETERMINING COPPER.<sup>1</sup>

BY W. E. GARRIGUES.

Received October 26, 1897.

JUDGING by the number of articles that continue to appear from year to year in chemical journals, elaborating more or less complete schemes for the analysis of these alloys, the subject is still a timely one for discussion. There is, furthermore, small likelihood that this apparent interest will lag, in the near future at least, owing to the evident fact—and it is one that must not be lost sight of in passing judgment on the merit of such a combination of methods for separation and determination as the present paper deals with—that we are not considering a material capable of being handled like steel, where accurate methods have been found for ascertaining the quantity of almost every element present without the necessity of first removing three or four others from solution.

In the light of our present knowledge of the chemical deportment of the metals of the hydrogen sulphide and ammonium sulphide groups, all methods which even approach accuracy must of necessity be comparatively tedious. Not alone is it essential in almost every case to free a solution from interfering elements to reach the one sought, but in very many instances it is all but impossible to get the former out of the way without sustaining loss of the latter. Add to this the manipulative difficulties such as the washing of slimy precipitates that persist in

<sup>1</sup> Read before the Chemical Section of the Engineers Society of Western Pennsylvania.

passing the filter medium, and those that in coming down occlude non-volatile salts used as reagents or sustain loss in ignition through reduction and volatilization—there is certainly sufficient difficulty remaining to interest many of us for years to come.

The present paper is not written so much with the object of presenting innovations that conduce to speed as to discuss some of the inaccuracies in very commonly used processes and to consider means for overcoming them, even though at times additional labor may be involved. Of late years the art of successfully working scrap has reached such perfection that it is probably not an error to assume that the greater part of the metal in alloy bearings now in use, was at one time doing duty along a varied line reaching from wash-boiler bottoms to tea packages. The inevitable result is that the subject has grown still more intricate from the analyst's point of view, the range of elements existing in small percentages being greater.

The alloys considered are bronze, brass, and white metal, composed of copper, tin, antimony, lead, zinc, iron, phosphorus, and arsenic.

The advantage of a qualitative analysis previous to beginning the analysis proper, has often been dwelt upon, and there is but little doubt that it almost invariably repays the trouble tenfold. In the scheme to be outlined here it is particularly desired to know beforehand whether antimony, iron, zinc, and arsenic are absent; for this purpose we have found the following procedure easy and satisfactory. The sample is oxidized with nitric acid and evaporated dry, boiled with a little dilute nitric acid, the residue filtered out and washed.

*Antimony.*—Ignite a portion of the residue intensely, boil with strong hydrochloric acid, and dilute with an equal volume of water. Filter and add considerable water, when a white precipitate indicates antimony. Confirm by orange hydrogen sulphide precipitate.

*Arsenic and Iron.*—The remaining portion of the residue is warmed with a little caustic soda solution and dissolved by the further addition of alkali sulphide and heating. The black residue is removed by filtration and treated for iron by any suitable

method. In the alkaline filtrate arsenic is precipitated with ammonia and magnesia mixture, the precipitate filtered out and dissolved in hydrochloric acid, which solution is boiled with sulphurous acid, and then saturated with hydrogen sulphide, when the arsenic, if present, is obtained as sulphide.

*Zinc.*—The filtrate from the nitric acid insoluble residue is saturated with hydrogen sulphide, the filtrate mixed with one-tenth its volume of strong hydrochloric acid, and potassium ferrocyanide added, when zinc is indicated by a white precipitate of the ferrocyanide.

Quite a large amount of the sample should be used, as otherwise antimony may all pass into the nitric acid filtrate and thus escape detection. The ignited stannic oxide is entirely insoluble in the boiling hydrochloric acid, while sufficient antimony dissolves to give ample reactions. The large amount of hydrochloric acid is added previous to testing for zinc, to prevent the coprecipitation of any lead that may have escaped coming down as a result of the hydrogen sulphide treatment.

Coming now to the quantitative part of our subject, we have to consider first

#### THE DETERMINATION OF SINGLE ELEMENTS.

Zinc, when present in fairly large quantity, and an absolutely correct determination is not required, can be very conveniently measured by titration with standard potassium ferrocyanide, but in smaller amounts a gravimetric method is preferable. For the details of the process, see Stone.<sup>1</sup> The end point is marked by an immediate green color with cobalt nitrate.

Stone directs that the volume of standard liquor necessary to give the end reaction be determined by a blank experiment, and that this amount be subtracted from each titration. This statement we have been entirely unable to verify, as witness the following set of titrations of varying amounts of the same solution of zinc chloride :

<sup>1</sup> This Journal, 17, 413.

| Zinc chloride.<br>cc. | Potassium<br>ferrocyanide.<br>cc. | Total<br>Per cent. | Blank<br>Per cent. |
|-----------------------|-----------------------------------|--------------------|--------------------|
| 0                     | 1.5                               | ....               | ....               |
| 5                     | 6.0                               | 30.0               | 22.5               |
| 10                    | 11.8                              | 29.5               | 25.7               |
| 12.5                  | 14.6                              | 29.2               | 26.2               |
| 15                    | 17.5                              | 29.15              | 26.6               |
| 25                    | 29.2                              | 29.2               | 27.7               |

Total per cent. column is figured on the assumption that the highest titration is per cent. zinc, the lower titrations then being multiplied to equal the same volume of zinc chloride used—no blank being subtracted. Figures in blank per cent. column are obtained in the same manner except that the blank is in each case subtracted. It will be noticed that the figures in the latter column are anything but uniform among themselves. To get the best results the standard solution should be titrated against a known zinc solution of the same strength as the sample under examination. In applying the process absence of copper and iron is essential.

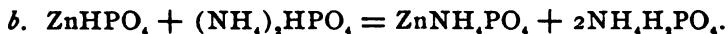
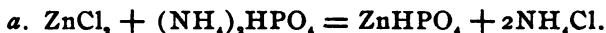
When the conditions of precipitation are fully understood one of the neatest and most accurate analytical processes is the determination of zinc as phosphate. All metals, inclusive of alkalies, should be absent.

The solution should be exactly neutralized with hydrochloric acid or ammonia, as the case may be, using methyl orange as indicator, unless the liquid contains acetic acid, in which case no further inconvenience results except that litmus is substituted for methyl orange. A very large excess of ammonium phosphate is to be avoided, as otherwise the precipitate is redissolved to some extent. This part of the process is, however, not the delicate matter it might seem from the statement, as will be shown later. The most satisfactory mode of procedure is to add first say one gram of the phosphate, which will not hold up the smallest traces of zinc, and if a large precipitate comes down, to continue the addition. Hydrogen sulphide should give no trace of precipitate in the filtrate. It is highly advisable to work only with ammonium salts from the beginning, sodium salts being less good, and potassium salts entirely prohibited as they are carried down with the precipitate by occlusion in astonishing amounts.

The ammonium phosphate is added to the warm solution of the zinc, which is then further warmed until the precipitate is entirely free from any flocks and the solution has completely cleared. Filtering on a Gooch crucible, washing with water and then alcohol, drying at 100° C., and weighing as zinc ammonium phosphate is recommended. Using an ordinary filter paper and igniting seems to cause an unavoidable loss through reduction, no matter what care be exercised in separating the filter. It may, however, be ignited with perfect safety on a Gooch, even though a disk of paper be used as the filtering medium. In the latter case the paper should be turned above the precipitate toward the mouth of the crucible.

The details of the method, with sodium phosphate as precipitant, appear in the last edition of "Crookes' Select Methods." The original author's statement that the ignition gives low results owing to volatility of the zinc pyrophosphate cannot be admitted, in fact our excellent results obtained by ignition on a Gooch prove that such is not the case. The same applies to his claim that the precipitation takes place in an acid solution.

Though a difference of opinion as to what constitutes an acid solution may in some cases exist, it certainly does not seem reasonable to apply the term to a liquid smelling strongly of ammonia. The reactions occurring are probably expressed by the equations



It is even likely that these two stages are entirely separate, since in a cold solution the precipitate is at first as flocculent as an alumina precipitate, while on warming it becomes as dense as barium sulphate. If only the amount of ammonium phosphate called for by the first equation is added, the precipitate remains flocculent despite continued heating.

The double equation requires nearly five parts ammonium phosphate for one part zinc and we have successfully thrown down two-tenths gram zinc with one gram of the phosphate obtaining it all as the ammonium salt. The same quantity was also perfectly precipitated with five grams of ammonium phos-

phate but eight grams left a little zinc in solution. Similarly, 0.008 gram was completely thrown down with 0.05 and 3.00 grams, respectively, while five grams caused some re-solution.

Returning to the question of acidity, it will be seen from the equation that monoammonium phosphate remains as a product of the reaction but the excess of the diammonium phosphate, always used in practice, decomposes on heating to monoammonium phosphate and free ammonia, thus determining the alkalinity of the liquid. The precipitate is soluble with great facility in any kind of acid or in excess of ammonia. Too much cannot be said in favor of the process for accurate work.

Copper is determined in smaller quantities by the iodide method and in larger quantities by the new process described below. The latest literature added to the iodide method is Low's paper.<sup>1</sup> He introduces two modifications: Oxidation of any arsenic present with potassium chlorate and neutralization of the excess of nitric acid with zinc acetate.

There is no doubt, as Low states, that the end point is better as a result of the use of zinc acetate than when the sodium salt is employed; the oxidation with chlorate is also a great step in advance for the process. It is, however, a mistake to use any acetate as the end point is then at best not clear, though with practice it can be distinguished.

Some time ago the writer had the honor to present to this section a paper on the iodide method for copper, in which it was proposed to avoid the inaccuracy introduced by the presence of arsenic by separating the copper from it with glucose in the well-known manner. The object was to retain the clear end point when the titration is conducted in a very slightly acid sulphuric acid solution. Since that time the following, relative to the subject, has been ascertained:

When copper and arsenic, either as metals or sulphides, as obtained in the course of analysis, are dissolved in nitric acid, there is very apt to result a solution of the arsenic both as arsenic and arsenious acid. If now this solution be boiled with chlorate in a fairly concentrated condition, all the arsenic is oxidized to the higher form. Arsenic acid in strongly mineral acid solution, mixed with an iodide, is reduced to arsenious acid

<sup>1</sup> This Journal, 18, 458.

with liberation of iodine, causing the result for copper to appear high. In a solution which is, however, only faintly acid from a mineral acid, this reaction does not take place, in fact free iodine will then even oxidize arsenious acid to some extent but far less so than in acetic solution. In the presence of little acid and arsenious acid the result for copper would therefore appear low, since the iodine liberated by the copper would be in part consumed by the arsenic instead of being measured by the titrating liquid. If the copper solution be only faintly acid and the arsenic all present as arsenic acid, an accurate result for copper is obtained in sulphuric acid solution and the end point with starch is vastly superior than if either zinc or sodium acetate has been used.

The thiosulphate solution should be standardized on approximately the amount of copper found in the assay, conveniently obtained by measuring out a standard copper sulphate solution, if the best results are to be gotten. In the writer's experience a little more than the theoretical amount of iodine is liberated, and this not in absolutely uniform ratio. For small amounts of copper it is advisable to allow the solution to stand a given time, say ten minutes, between the addition of the iodide and the titration, otherwise the end point will come and go in a rather unsatisfactory manner.

While the method is good, very much to be preferred to the cyanide titration of Parks and Mohr, after an extended experience with it we must certainly dissent from Low's claim of superiority for it as against the electrolytic assay.

#### NEW PROCESS FOR COPPER.

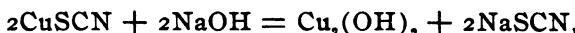
This depends on the precipitation of the copper as cuprous thiocyanate according to Rivot, and the alkalimetric determination of the combined thiocyanic acid.

The solution is evaporated with as little sulphuric acid as possible to expel any volatile acids; warm gently after dilution, and add sulphurous acid until its presence is plainly apparent by odor. Precipitate with an alkali thiocyanate. When the liquid settles perfectly clear, which is promoted by further warming, filter and wash well with water.

Transfer the filter and contents back to the beaker in which the precipitation was effected, boil with a measured excess of

standard caustic alkali, a few minutes is sufficient, then cool and dilute to a convenient bulk (200 cc.). After passing through a dry filter, take of the filtrate a quantity equal to one-half the bulk of the original solution, and titrate to neutrality with standard acid and methyl orange.

The rationale of the process is that caustic alkali converts cuprous thiocyanate into cuprous hydroxide and alkali thiocyanate, the latter body being neutral to methyl orange. The reaction proceeds quantitatively according to the equation



with all quantities of copper, one equivalent of caustic soda equaling one of copper. No requirement of an empirical standard is one of the advantages of the process. The writer claims for it greater accuracy than the iodide method is capable of.

Antimony is determined by Mohr's method: titration with iodine in alkaline solution, antimonous acid being previously reduced by the method of Gooch and Gruener.<sup>1</sup> This is very much to be preferred to the oxidimetric method again recently advocated by Thompson,<sup>2</sup> or to any attempt at separation from tin.

Lead is determined as sulphate, filtering on a Gooch with a paper disk, drying and weighing. In this manner the determination is capable of great accuracy, the drying being much better than ignition.

Tin is weighed as oxide, or in presence of antimony is determined by difference in weight.

Arsenic by Lundin's distillation process as described by Blair in his work on iron analysis.

Phosphorus as magnesium pyrophosphate.

#### GENERAL CONSIDERATIONS.

When an alloy is treated with nitric acid, a more or less white residue remains insoluble. This contains all the tin, part of the antimony, iron, arsenic, phosphorus, copper, and lead, the two last of course only in small amount though the copper may amount to several milligrams. No method of treatment has

<sup>1</sup> *Am. J. Sci.*, 42, 233.

<sup>2</sup> *J. Soc. Chem. Ind.*, 15, 255.

been found which gives this residue free from iron and copper. If all excess of nitric acid be evaporated and the residue again taken up with dilute nitric acid it is possible to retain all the iron in the residue, provided the tin is present in fair amount. The same applies also to the arsenic and antimony, though it is probably unsafe to count on this. In no event can the insoluble residue from a brass or bronze be considered sufficiently pure to weigh as stannic oxide. We separate the iron, copper, and lead from the tin and antimony by fusing with sodium thiosulphate and dissolving in water, preferring this to attempting to make the usual alkali sulphide separation in solution with all the copper and lead. The thiosulphate is a neater and quicker flux than sodium carbonate and sulphur.

If to save time in determining tin alone, when phosphorus, arsenic, and antimony are absent, it is desired to obtain the weight of stannic oxide by difference, the nitric acid insoluble residue may be ignited and weighed, fused with thiosulphate, dissolved in water, and the sulphides of lead, copper, and iron remaining, removed by filtration. The filter is then moistened with nitric acid and ignited in the same crucible (the fusion does not alter its weight perceptibly), subtracting the weight so found from the total weight of the residue. The difference is taken as stannic oxide.

A slight error must, however, be noted here: any lead present was weighed first as oxide and afterwards subtracted partly or wholly as sulphate. It may be present to an extent that will make this error serious. If, on the other hand, the sulphides are not moistened with nitric acid, the iron is very likely to burn only to the magnetic oxide, where it was at first weighed as the peroxide, while the condition of the lead is indefinite.

In the case of a complete analysis of an alloy containing zinc it is a great help to get all the iron out of the way at this early stage, and as the copper and lead must be returned to the main solution it will be more troublesome to separate these after igniting the sulphide precipitate than to precipitate the tin directly as sulphide from the solution of the fusion, and converting to oxide for weighing. The latter also has the advantage that it is applicable in the presence of phosphorus.

Hempel,<sup>1</sup> referring to the separation of phosphorus from tin, states that some of the phosphorus invariably comes down with the hydrogen sulphide precipitate of the tin. Whether or not the same applies to the sulphide precipitate obtained as a result of acidulating the dissolved fusion we have not ascertained, but it seems probable that it would not. At any rate the amount is too small to practically affect a tin determination in phosphor bronze. Arsenic, however, will largely remain with the ignited tin precipitate unless previously separated.

When the nitric acid filtrate from the insoluble residue is evaporated with a little sulphuric acid to take out the lead, there results a further precipitation of antimony. The lead sulphate cannot be removed by solution in ammonium acetate, as the antimonic acid is likewise affected. A large excess of sulphuric acid prevents this second precipitation, but its presence is undesirable for the separation of copper as thiocyanate. A little tartaric acid added to the diluting water will also prevent it, and has, moreover, no effect on the copper precipitate, but this may cause the re-solution of a trace of lead. For ordinary purposes this amount is negligible, but at any rate it may be very easily recovered and added at a later stage.

Alloys containing antimony are usually poor in copper and free from zinc; exceptions, however must be allowed for, and in the presence of both zinc and antimony the precipitation of copper as thiocyanate is not advisable, as the scheme thereby becomes complicated. Instead, the excess of sulphuric acid is used to prevent the precipitation, with the lead sulphate, of any antimony that remains in the nitric acid solution. In the filtrate from the lead sulphate the antimony and copper are thrown down together as sulphides and separated with caustic soda. In the residue the copper may, of course, be determined by the thiocyanate process, but as it is free from any other metals it is directly available for titration by the iodide method. In the filtrate from the sulphides the zinc is obtained as phosphate. It should be remembered that if great accuracy is desired in the figure for zinc, the sulphide precipitate, after removing the antimony, is to be dissolved and again precipitated to insure against loss of zinc.

<sup>1</sup> *Ber. d. chem. Ges.*, 22, 2478.

As a result of converting the mixed sulphides of tin and antimony into oxides for weighing, a slight error is sustained owing to the fact that the two sulphides require different treatment to give accurate results. By treatment with fuming nitric acid combined sulphur is oxidized completely and the full heat of a good Bunsen burner will convert all pentoxide of antimony to tetroxide without any trouble, but while the tin precipitate requires a white heat to drive out the last traces of water, antimony will not stand this heat. If, therefore, the Bunsen flame be used and one-tenth per cent. be subtracted from each twenty per cent. of tin found, the result is better than if the actual weight obtained is taken.

As the sulphides of tin and antimony are recovered from the dissolved fusion, they are mixed with considerable free sulphur which cannot be completely oxidized with fuming nitric acid in one evaporation. For the most careful work, washing the dried sulphides with carbon disulphide is necessary, but ordinarily, careful ignition will answer. After evaporating the mass to dryness with fuming nitric acid and burning at a temperature just sufficient to ignite the sulphur, the residue is again moistened with fuming nitric acid for final ignition. This is important. The paper is, of course, to be consumed separately. A well-rounded, inverted lid is used as a cover during the action of the acid.

When the ignited oxides of tin and antimony are dissolved by fusion with caustic (or carbonated) alkali and obtained as higher chlorides in acid solution, potassium iodide reduces only the antimonous salt. We prefer to boil down twice to about fifty cc. to insure the expulsion of the liberated iodine. We have found the color of the liquid not a safe guide in practice except that if perceptible deepening of the yellow takes place when approaching the bulk mentioned, the liquid must be immediately diluted and the second evaporation not carried quite so far. Failure to do this will result in loss of antimony by volatilization.

The separation with hydrogen sulphide of copper from zinc in hydrochloric acid is, according to Fresenius, rarely perfect. On testing a number of copper sulphide precipitates from solutions of brass containing fifteen cc. strong hydrochloric acid in a bulk of 200 cc. of liquid, we have never failed to find zinc in appreciable quantity. The precipitation as thiocyanate is, on the other

hand, absolutely free from this source of error ; and if the volatile acids are expelled with as small a quantity of sulphuric acid as possible, the amount of copper that escapes precipitation is infinitesimal. The precipitate cannot be dried and weighed with anywhere near the accuracy one might be led to suppose from the single experiment quoted by Fresenius. Such a procedure is quite out of the question.

The excess of ammonium thiocyanate exerts no deleterious action on the zinc precipitation with ammonium phosphate in the filtrate, and methyl orange is available as indicator for exactly neutralizing the solution. When potassium thiocyanate is used the zinc precipitate is highly contaminated, so much so that it fuses at a low heat to a clear liquid, the results being entirely without value.

THE ANALYSIS OF BRONZE AND BRASS. (ANTIMONY BEING ABSENT.)

Oxidize one gram with strong nitric acid and evaporate on the water-bath to complete expulsion of the acid. Take up with fifty cc. three per cent. nitric acid and filter after boiling five minutes. Ignite filter and contents together in a porcelain crucible, grind the residue with a thick glass rod, and fuse with a liberal addition of sodium thiosulphate. Leach out with a little water, digest until the liquid is clear yellow, and remove the precipitated sulphides by filtration. In the absence of arsenic, determine tin in the filtrate by acidulating with hydrochloric acid, filtering out the sulphide of tin, and washing with ammonium acetate. Ignite at low temperature, together with the filter, raising the heat gradually after all free sulphur has been consumed, and finishing with a blast to constant weight.

The mixed sulphides of lead, copper, and iron, recovered from the fusion, are dissolved by boiling with twenty per cent. nitric acid, from which solution the iron is thrown down by ammonium acetate. The filtrate is added to the main solution and the whole evaporated with as little sulphuric acid as possible, the lead sulphate collected on a Gooch crucible, and weighed.

In the filtrate the copper is thrown down as thiocyanate and its value determined by the method described. The zinc is then

obtained from the neutralized filtrate with ammonium phosphate, observing the precautions mentioned.

Phosphorus is determined in a separate portion by heating some time with aqua regia, passing hydrogen sulphide into the alkaline solution, and filtering. The phosphorus is then obtained with magnesia mixture as usual. If qualitative tests have shown presence of arsenic the magnesia precipitate is dissolved in hydrochloric acid, arsenic reduced by boiling with sulphurous acid, and precipitated with hydrogen sulphide. In the filtrate the phosphorus is obtained with molybdate and the yellow precipitate weighed, after collecting on a Gooch crucible with a paper disk.

Arsenic is determined in a separate portion by Lundin's method, just as described by Blair, except that we deem one evaporation to dryness with sulphuric acid sufficient.

In the tin determination, arsenic is separated from the solution of the thiosulphate fusion with magnesia mixture, the tin being then obtained in the filtrate as described.

In the analysis of brass, a more rapid, but not so accurate, determination of the copper and zinc may be obtained by using the iodide method for the former and the ferrocyanide method for the latter. The foregoing process is carried out to the point of obtaining the filtrate from the lead sulphate. This is mixed with about ten cc. hydrochloric acid and the copper precipitated by boiling a few minutes with strips of sheet aluminum. For a neat manner of treating this copper, consult Low's paper already referred to.

The filtrate is ready for titration of zinc with ferrocyanide according to Stone.

#### THE ANALYSIS OF WHITE METAL. (ANTIMONY BEING PRESENT.)

Proceed as in analysis of bronze up to the point of evaporation with sulphuric acid to remove lead, but in this case use about fifteen cc. of acid instead of about two. Dilute with eighty-five cc. water and filter without unnecessary delay or boiling. Dry and weigh the lead sulphate.

Copper and antimony are thrown down in the solution with hydrogen sulphide, and after boiling the filtrate free from the

gas and oxidizing any fine sulphur with nitric acid, zinc is obtained as phosphate in the neutral solution.

The sulphides of copper and antimony are washed from the filter back into the beaker, boiled with a little caustic soda which is passed through the filter, and the filtrate now containing the antimony is added to the solution of the thiosulphate fusion of the nitric acid insoluble residue. The remaining copper sulphide is dissolved by boiling it in 1.20 sp. gr. nitric acid, when it is neutralized and the copper determined with potassium iodide and thiosulphate.

The alkaline solution, containing now all the tin and antimony, is acidulated with hydrochloric acid and the mixed sulphides filtered out. Ammonium acetate is used for washing as before, but the paper is separated from the dried precipitate and burned alone, followed by the precipitate itself. Ignite in the manner already described for antimony and tin sulphides in the presence of free sulphur. Having obtained the weight of the mixed oxides, it now remains only to determine the antimony, which is attained quite accurately, as follows:

Grind the residue in the crucible and pour the powder into a silver crucible containing about six grams of previously fused caustic potash. Reweigh the porcelain crucible to ascertain the amount of the residue actually taken for antimony, of course making correction for the difference later.

When fused, dissolve in water, add five grams tartaric acid and dilute hydrochloric acid to neutrality. Wash into flask and add five cc. strong sulphuric acid and one and a half grams potassium iodide, keeping the solution down to a bulk of 100 cc. as nearly as possible. Boil down rapidly to about fifty cc., observing the precautions already referred to, dilute with boiling water to about 100 cc., and boil down again to about fifty cc. The antimony is now all reduced.

Cool, add a pinch of dry phenol phthalein and caustic soda to alkalinity. Discharge the red color with dilute hydrochloric acid, cool again, add starch paste and fifty cc. saturated sodium bicarbonate and titrate with decinormal iodine solution to appearance of the blue color. We find that by working in this manner one cc. of the iodine is equivalent to 0.00615 gram antimony. Theory requires 0.0060.

The tin is obtained by the difference in weight, calculating the antimony to  $Sb_2O_3$ . From every 20 per cent. tin so obtained, subtract one-tenth per cent., as explained previously.

In conclusion, we may add that any scheme which ignores the antimony passing into the nitric acid solution when the alloy is oxidized, is not worth considering. Working on one gram it amounts to from three to four per cent. of antimony, calculated on the alloy. Some results point to the feasibility of making correction for this solubility instead of holding back the main precipitate for it.

THE DUQUESNE CHEMICAL LABORATORY,  
PITTSBURG, PA.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 24.]

### THE CONSTITUTION OF ARSENOPYRITE.

BY F. W. STARKE, H. L. SHOCK, AND EDGAR F. SMITH.

Received October 30, 1897.

THIS mineral is generally described as a sulpharsenide of iron. It has never been determined in what state of oxidation the iron exists, although it is customary to express the composition of the mineral by the formula  $FeSAs$ , in which some chemists have thought that the arsenic functions as a dyad element, that arsenopyrite consequently is nothing more than ordinary pyrite, in which an atom of arsenic has replaced an atom of sulphur, or that it is an iron arsenide in which sulphur, acting with a valence of three, has replaced arsenic. There is no experimental evidence favoring either assumption.

Pyrite and marcasite have been studied with the view of ascertaining the condition of the iron in them.<sup>1</sup> It was discovered that the first contained about one-fifth of its total iron content in the ferrous condition, whereas all the iron in marcasite existed in the ferrous state. Subsequent experiments have amply confirmed this observation. Efforts were also made to determine the nature of the iron in arsenopyrite.<sup>2</sup> These resulted negatively.

The present communication presents experimental results

<sup>1</sup> A. P. Brown: *Am. Phil. Soc. Proc.*, 1894.

<sup>2</sup> T. M. Lightfoot: This Journal, Sept., 1894.

obtained during the last few years. These in no wise conclusively prove the constitution of arsenopyrite, but they do furnish data which in the future, perhaps, may prove helpful in the solution of the chief problem.

One of the first steps undertaken was the exposure of arsenopyrite to a current of hot hydrogen. The mineral was placed in a porcelain boat, contained in a combustion tube, and gently heated while the gas passed over it, care being taken that the temperature did not become so great as to break down the hydrogen sulphide produced in the experiment. Some arsenic was also volatilized. Repetitions of the experiment were made and the escaping gases were collected in receivers containing hydrochloric acid and bromine. The sulphur expelled in this manner equaled 19.92 per cent. Perfectly pure arsenopyrite, FeSAs, contains 19.63 per cent. of sulphur. Here then we have evidence of the quantitative expulsion of the sulphur content. The contents of the boat showed arsenic and iron. The traces of the former observed over the boat and in the tube indicate that the arsenic was not so readily separated from its union with the iron, and therefore we may justly infer that the sulphur was less intimately combined. Returning to pyrite and marcasite, we found that they also, when heated in an atmosphere of hydrogen, lost one atom, or one-half, of their sulphur. This would be fair evidence for the assertion that a sulphur atom in each of these bodies was less intimately combined, and this would argue for a similarity of these minerals in this respect.

Arsenopyrite was next intimately mixed with dry ammonium chloride and heated in an atmosphere of pure nitrogen. On dissolving the boat contents in water and applying suitable tests much ferrous iron was indicated, and at the same time evidences of ferric salts were distinctly observed. As nothing definite in regard to quantity could be ascertained in this way, portions of finely divided mineral were heated with copper sulphate, of varying strength, in sealed tubes. A number of complete decompositions were obtained, but on attempting to titrate the ferrous iron with potassium permanganate, as had been done with marcasite, more iron was found than the mineral actually contained. This meant that some other reducing agent than ferrous salts was present. And in this instance it was no doubt

arsenious oxide. This procedure could not, therefore, be regarded as sufficiently reliable to afford an idea of the correct amount of iron in the ferrous state. It served merely to further substantiate the hint gained by heating the mineral with ammonium chloride.

Experiments made upon the direct action of gaseous haloids on sulphide of arsenic proved that the latter was wholly volatilized. It was, therefore, natural to suppose that these reagents might possibly eliminate arsenic from its naturally occurring compounds. To this end hydrogen bromide, which had been conducted over red phosphorus and phosphoric anhydride, was passed in the cold over a boat containing finely divided arsenopyrite. At first there was no apparent action. On applying a very gentle heat a yellow-colored sublimate appeared in the cooler portions of the tube. The boat contents became crystalline and yellowish-green in color. Both ferrous and ferric iron were found, the latter, however, in not very great amount. Several quantitative trials were made:

*Experiment 1.*—0.2395 gram of material heated in hydrogen bromide gave a product soluble in water. When the aqueous solution was titrated with potassium bichromate, it showed the presence of 28.71 per cent. of iron in the ferrous state.

*Experiment 2.*—0.1507 gram of the material treated as in 1, gave 27.93 per cent. of ferrous iron.

*Experiment 3.*—0.1720 gram of the arsenopyrite, treated as in 1 and 2, showed 26.11 per cent. of iron in the lower state of oxidation.

The variation in the ferrous content in these three trials can easily be explained. To effect the complete decomposition of the mineral, it was necessary to raise the temperature, and this was attended by a slight dissociation of the hydrogen bromide and a consequent partial oxidation of the iron. The experiments, however, possessed value, as they helped to confirm previous efforts in that they showed the presence of a predominating quantity of iron in the lower state of oxidation.

We next resolved to substitute dry hydrogen chloride gas for the hydrogen bromide. When this was done arsenic chloride and a little ferric chloride were carried over into the receiver. The boat contents were white in color and dissolved completely

in water. Some quantitative determinations were made as described under the hydrogen bromide decompositions.

*Experiment 1.*—0.0682 gram of arsenopyrite, when heated in hydrochloric acid gas, left a residue in the boat, which was soluble in water, and when the aqueous solution was titrated 30.86 per cent. of ferrous iron was found.

*Experiment 2.*—0.1332 gram of the material under similar treatment showed 30.55 per cent. of ferrous iron.

*Experiment 3.*—0.1675 gram of substance subjected to the same treatment as in 1 and 2, gave 30.16 per cent. of iron in the lower state of oxidation.

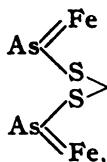
These results are concordant and may be accepted as showing the probable amount of ferrous iron in arsenopyrite, the total iron content of which is 34.35 per cent. This would leave about four per cent. of the iron existing in the ferric condition.

The arsenic collected in the receiver gave an immediate precipitate on the addition of hydrogen sulphide, thus arguing for the trivalent condition of that metal. Further, no precipitation occurred with a "magnesia mixture," evidence again of the absence of quinquevalent arsenic, and lastly, in all the complete decompositions of arsenopyrite brought about by copper sulphate, the consumption of potassium permanganate was far in excess of what was required by the iron, even if all of the latter had existed in the ferrous state. It is, therefore, reasonable to assume that arsenic in the trivalent condition was the cause of the excessive reduction, as no other reducing agent was present.

The facts fairly well established by the preceding experiments are: (1), that about seven-eighths of the total iron content represent ferrous iron, the remaining eighth being ferric iron; (2), that the total arsenic is in the trivalent condition. The readiness, furthermore, with which all of the sulphur is removed by hydrogen, would argue for a less intimate union of this element, and indeed that it is scarcely likely that it is in direct combination with the iron.

Any attempt to graphically represent these conditions must be regarded as entirely tentative and indeed speculative in the highest degree. The facts can be empirically represented in the formula  $14\text{Fe}''\text{As}''\text{S}.2\text{Fe}''\text{As}''\text{S}$ , beyond which we are not justified in going. However, were it not for the slight ferric

content, the constitution of arsenopyrite might be graphically written



and all the conditions of experiment fully satisfied. We cannot expect much from such speculative formulas, until we have better and satisfactory evidence in regard to the size of the molecule. Until methods have been devised for the determination of the molecular magnitude of minerals, it will be wiser to merely state the facts, leaving it to future workers to collate them. It may not perhaps be out of place to observe that we endeavored to discover some suitable means of determining mineral molecular magnitudes, but we are still destitute of anything approaching even an approximate method. We sought to learn what influence a weighed quantity of arsenopyrite would exert upon the solidification point of low fusing alloys, *e.g.*, Rose's metal, Wood's metal, without arriving at anything definite. And in the case of certain related minerals (marcasite and pyrite) specific heat and electric conductivity experiments were carried out in the hope of detecting differences connected with varying constitution, but such proved not to be the case.

UNIVERSITY OF PENNSYLVANIA.

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### ESTIMATION OF MINERAL MATTER IN RUBBER GOODS.

BY L. DE KONINGH.

Received October 29, 1897.

IT is a well known fact that the amount of mineral matter in rubber goods cannot be determined by means of a simple ignition, as the ash does not represent the original mineral matter. For instance, white lead becomes lead oxide, chalk is largely reduced to calcium oxide, some oxides volatilize, etc. By using the following process the writer believes he has effected a decided improvement. Five grams of the very finely divided sample are treated in a covered beaker with fifty cc. of fuming hydrochloric acid, and after soaking for an hour, the

whole is heated up to  $70^{\circ}$  for another hour. Fifty cc. of water are then added, and the insoluble matter is collected on a filter. The washing with boiling water takes some time, as the acid causes the rubber to swell out to an enormous extent; however, after a liter of water has been used the washings are generally free from acidity. The residue is now carefully transferred from the filter into a weighed porcelain dish; no practical difficulty will be experienced in this operation. After drying on the open water-bath until no more water-vapor is visible, the dish is placed inside an air-bath and heated for three hours up to  $105^{\circ}$ . After cooling it is weighed, and the result is the rubber minus the greater part of its soluble ash. The remainder of the ash is then found by an ignition. Some samples examined by the writer, which gave on simple ignition about fifty per cent. of ash, gave only ten per cent. after the acid treatment, and the ash was then found to consist chiefly of barium sulphate. If it be desired to distinguish between heavy spar and silicates, the writer still uses a process described by him some years ago, based on the fact that barium sulphate is soluble in hot sulphuric acid, and may be completely reprecipitated on adding water.

The acid filtrate may, if desired, be subjected to further analysis.

Before recommending the process it was necessary to ascertain if the strong acid dissolves any organic matter. If the filtrate is evaporated nearly to dryness after having added a few cc. of sulphuric acid, there is obvious darkening, and an unpleasant albuminous odor is noticed. But, as will be seen, the loss is not very great, and may even to some extent be allowed for. Five grams of a block-rubber containing forty per cent. of ash were treated with fifty cc. of fuming hydrochloric acid at  $70^{\circ}$ ; fifty cc. of water were then added, and after standing for several hours, fifty cc. of the filtrate were diluted with 450 cc. of water and thirty grams of crystals of magnesium sulphate were added on account of the presence of hydrochloric acid. Standard solution of potassium permanganate (0.001 gram oxygen per cc.) was added until the liquid turned pink, and more was added during the next half hour; each time the color began to fade. Three cc. of permanganate were thus consumed. To ascertain how

much organic matter this represents, 0.03 gram of a dry albuminoid (peptone) was dissolved in twenty-five cc. of fuming hydrochloric acid and then titrated with permanganate in exactly the same way ; the result was also three cc.

By an easy calculation it follows that five grams of the block-rubber had yielded to the acid about 0.06 gram of organic matter, or about one per cent.

LONDON, ENGLAND, OCTOBER, 1897.

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#### OBITUARY.<sup>1</sup>

**DR. MEINHARD ALSBERG.**—The colleagues and many friends of Dr. Meinhard Alsberg were startled by the news of his sudden and unexpected death in the Adirondacks, while on a visit to his family on September 7th, for though somewhat delicate in appearance, he had impressed all who knew him as one endowed with a good constitution.

Dr. Alsberg was born in 1842, a native of the small German State of Waldeck. Until his fifteenth year he went to the Gymnasium at Korbach, but then was put by his father to a commercial business. This, however, was so much against his inclinations, that he was sent to the Polytechnic at Braunschweig, where on graduating he was awarded a special prize, which induced his uncle to furnish the funds for his university education. He studied at first at Göttingen, and later in Jena, where he graduated in 1864, and became assistant at the University laboratory. In 1865 he came to New York. The friendship of his celebrated teacher, Prof. Wöhler, earned him his first position here soon after his arrival. But he looked upon these positions merely as stepping stones for what he considered his real calling—a manufacturing chemist. His first venture in this direction, the manufacture of lactin, he was soon compelled to give up on account of lack of capital.

He then in 1868 commenced the manufacture of vermillion. He was the pioneer of the successful manufacture of vermillion in this country, and his achievements soon brought him the necessary capital to make the business a paying one. For six

<sup>1</sup> Read before the New York Section, October 15, 1897.

years, commencing in 1873, he merged his business in that of the Ansbach Manufacturing Co., whose manager he was. Since 1880 the firms, in which he was partner, were known successively as Sondheim & Alsberg, Sondheim, Alsberg & Co., and Alsberg & Pfeiffer.

He gradually widened the scope of his manufactures until they practically embraced most colors in ordinary use, and he did this single-handed, and not by the time-honored method of engaging a so-called specialist for a short time.

For this the chemists of our country should be especially thankful, for thereby he has demonstrated, that thorough scientific training, and the art of properly applying it, is the only real secret of success—a truth too often denied.

The *Oil, Paint and Drug Reporter* speaks of Dr. Alsberg as follows : Dr. Alsberg was an expert chemist, with a thorough knowledge of color and color-making, which contributed largely to the success of the firm with which he was connected. He stood high in the trade, and his death will be widely regretted." But though he was a business man, he never forgot science. He not only applied it profitably in his business, but he cultivated it for its own sake. His publications were not many, as is natural with a man whose time is fully occupied with the cares of a business, yet he did all in his power to aid others.

At the time when the *American Chemist* promised to become the *Chemical News* of this country, he belonged to the corps of abstractors, and as such, furnished not only abstracts, but verbal translations of important scientific papers.

Later, when the American Chemical Society was founded, we find him as one of the original eight, who signed the call to the chemists of this country. He was an active and enthusiastic member of the society, and did much for it in the early days of its existence, giving much of his time to drudgery in honorary positions, which the society now is able in some cases to fill by paid officers. He was also an enthusiastic worker for the Society of Chemical Industry.

Of his publications, the following may be mentioned :

In 1864 he published the results of his investigation on some

acrolein compounds, which formed the theme for his inaugural dissertation.

In the *American Chemist* we find two papers on the manufacture of vermillion. (Vol. 1, 205, and Vol. 3, 454.)

In the *Journal of the Society of Chemical Industry* he published a paper on Spontaneous Combustion. (Vol. 14, 947).

He was always ready to help and advise his friends. He was severely honest himself and expected that honesty in others.

H. ENDEMANN.

23 WILLIAM ST., N. Y.

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Commercial Fertilizers and Chemicals, and Other Information in Regard to Fertilizers. Bulletin No. 33. Season 1896-97. Department of Agriculture of the State of Georgia, Atlanta, Ga. 116 pp.

Winter Protection of the Peach. Peach Growing in Missouri. Bulletin No. 38. Agricultural Experiment Station of the University of the State of Missouri, Columbia, Missouri. 25 pp.

First Annual Report of the John Crerar Library for the year 1895. Chicago. 1897. 17 pp.

Second Annual Report of the John Crerar Library for the year 1896. Chicago. 1897. 21 pp.

The Chemical and Metallurgical Society of South Africa. Proceedings at the Monthly Meeting held on Saturday, September 18; 1897. The Rand Agency, Ltd, Secretaries, 37 and 38 Bettelheim Buildings, Johannesburg, S. A. R. 22 pp.

The Medico-Legal Journal. September, 1897. Vol. xv, No. 2. Published by Clark Bell, Esq., 39 Broadway, N. Y. \$3.00 per annum.

The Pharmacist at Work. By William C. Alpers. Philadelphia: J. B. Lippincott Co. 1898. pp. ix + 326. Price \$1.50.

Wheat.—1. Test of Varieties. 2. Test of Fertilizers. 3. Description of Varieties. 4. Treatment of Smut. Bulletin No. 69. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Kentucky, September 1897. 18 pp.

A Handbook for Chemists of Beet-Sugar Houses and Seed-Culture Farms. Containing Selected Methods of Analysis, Sugar-House Control, Reference Tables, Etc., Etc. By Guilford L. Spencer, D. Sc., of the U. S. Dept. of Agr. First Edition. New York: Jbhn Wiley & Sons. London: Chapman & Hall, Ltd. 1897. pp. x + 475.

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Issued with January Number, 1897.

## Proceedings.

### FOURTEENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The fourteenth general meeting of the American Chemical Society was called to order by the President, C. B. Dudley, in the Winslow Laboratory of the Rensselaer Polytechnic Institute, Troy, N. Y., Tuesday, December 29th, 1896, at 10.15 A. M.

President Dudley introduced the chairman of the local committee, Mr. Wm. A. Thompson, who, after a few remarks, presented the mayor of the city, Hon. Francis J. Molloy. Mayor Molloy gave a cordial welcome to the visiting chemists, and President Dudley followed with a brief response in behalf of the Society.

The regular program of papers and discussions was then taken up, a paper on "The Insoluble Carbohydrates of Wheat" being presented by H. C. Sherman.

This paper was discussed by Dr. Wiley, Mr. Griffin, President Dudley, and Mr. Sherman.

A paper on the "Velocity of the Reaction between Ferrous Chloride, Potassium Chlorate, and Hydrochloric Acid," was presented by A. A. Noyes and discussed by President Dudley, and Messrs. Hazen, Loeb, and Noyes.

The annual reports of the General Secretary, Treasurer, and Librarian were then presented, after which a short paper on "The Estimation of Boric Acid in Foods," by L. de Koningh, was read by A. A. Breneman, in the absence of the author. The paper was discussed by Messrs. Wiley and Breneman.

Some announcements were made by the Local Secretary, the President, and the General Secretary, after which the session was adjourned.

In the afternoon visits were made to the Troy Steel Co's works and to the U. S. Arsenal and Gun Factory at Watervliet.

The evening of Tuesday was devoted to a reception given to the visiting chemists by the local committee at the Troy Club.

Wednesday, December 30th, the Society was called to order by the President, in the Winslow Laboratory, at 10.15 A. M.

A paper on "The Examination of Municipal Water Supplies" was presented by Allen Hazen and discussed by Messrs. Mason, Hale, Phillips, Dudley, Breneman, Kennicutt, and Hazen.

Dr. H. W. Wiley presented a paper on "Basic Slags: Their Manufacture, Analysis, and Agricultural Value." This was discussed by Messrs. Dudley, McMurtrie, Griffin, and Sherman.

Vice-President Wm. McMurtrie, chairman of the New York Section, was called to the chair, and the President presented his annual address upon "Some Present Possibilities in the Analysis of Iron and Steel."

The President announced that there were enough papers that had not been read to warrant another session, but inasmuch as many of the chemists were obliged to go home early, he referred the matter to the Society to decide whether a third day's session should be held or not. After some discussion it was voted that the Fourteenth General Meeting should close with the present session, and that those papers which had not yet been read should be read by title and sent to the committee on Papers and Publications for the Journal.

The report of the canvassers of ballots in the annual election was presented and showed the following named officers chosen for the year 1897: President, Charles B. Dudley; General Secretary, Albert C. Hale; Treasurer, Charles F. McKenna; Librarian, F. E. Dodge; Councilors, John H. Appleton, Charles F. Chandler, Wm. McMurtrie, Charles E. Munroe; Directors, A. A. Breneman, Charles A. Doremus, Wm. McMurtrie, H. W. Wiley.

A paper by A. A. Blair on "The Determination of Sulphur in Pig Iron," was read by F. C. Phillips.

Upon motion of Wm. McMurtrie the thanks of the Society were extended to the local committee of arrangements for the meeting, the mayor and citizens of Troy, the Fitzgerald Bros., Earl & Wilson, Geo. P. Ide & Co., Major Isaac Arnold and the officers of the U. S. Arsenal at Watervliet, the Troy Steel Co., the Duncan Co. at Mechanicville, the Local Press, and the Troy Club.

(3)

The President then declared the Fourteenth General Meeting adjourned.

ALBERT C. HALE,

General Secretary.

SECRETARY'S REPORT FOR THE YEAR 1896.

*To the Members of the American Chemical Society:*

GENTLEMEN:—During the early part of the year 1896 there was, as usual, a considerable amount of routine work in connection with the organization of the standing committees for the year, the collection of annual dues, etc.

The summer meeting of the Society was held in Buffalo, N. Y., August 21 and 22, 1896, just before the meeting of the American Association for the Advancement of Science in the same city. At that meeting a joint committee from the American Chemical Society and Section C of the American Association for the Advancement of Science agreed upon the following recommendations as a means for bringing the summer meeting of the Society into closer relations with that of Section C.

I. Section C to have a business meeting for purposes of organization on Monday of the week of meeting, and the Vice-President's address to take place late in the afternoon of that day.

II. The American Chemical Society to be given Monday and Tuesday for their work.

III. Section C of the American Association for the Advancement of Science to be given the balance of the week.

IV. The arrangement of the program for the reading of papers before the two bodies to be left to the discretion of the President of the American Chemical Society and the Vice-President of Section C of the American Association for the Advancement of Science.

The committee appointed under a former administration to receive suggestions in regard to amendments to the constitution of the Society has continued its work during the year and will probably be able soon to present a unanimous report to the Council.

During the year the columns of the Journal have been filled with papers of a high order of excellence and the main difficulty has been to meet the expense of printing all that would enhance the value of the Journal to the members. The Society could use with advantage in this direction a much greater income than it

now has. It was suggested in a circular sent to the members some weeks ago that the most feasible means for obtaining the requisite funds and enlarging the sphere of influence of the Journal, is to make a concerted effort to increase the membership of the Society. There are still many chemists in the country whose names are not on our roll, and while there has been a very rapid gain in number of members during the past few years, there is no good reason why the membership, both active and associate, may not be even more rapidly increased.

The following statement shows the increase in membership since the Society adopted its present plan of organization and administration.

| Date.                | Members. | Associates. | Honorary members. | Total. |
|----------------------|----------|-------------|-------------------|--------|
| November, 1889.....  | 169      | 28          | 8                 | 205    |
| " 1890.....          | 203      | 27          | 8                 | 238    |
| " 1891.....          | 269      | 24          | 9                 | 302    |
| " 1892.....          | 319      | 25          | 7                 | 351    |
| September, 1893..... | 423      | 30          | 7                 | 460    |
| " 1894.....          | 664      | 50          | 8                 | 722    |
| " 1895.....          | 841      | 54          | 8                 | 903    |
| " 1896.....          | 911      | 65          | 7                 | 983    |
| December, 1896.....  | 939      | 65          | 7                 | 1011   |

The Society has lost by death the following named members and associates, not previously reported in the Secretary's Annual Statement.

- Eckley B. Coxe, Drifton, Pa., May 13, 1895.
- F. J. Ashcom, Riddlesburg, Pa., Oct., 1895.
- George T. Cooke, Boston, Mass., Nov. 4, 1895.
- Chauncey R. Stuntz, Cincinnati, O., Dec. 7, 1895.
- J. H. Westenhoff, Cincinnati O., Jan. 13, 1896.
- C. C. Hamilton, Kansas City, Mo., Mar. 10, 1896.
- Henry Bower, Philadelphia, Pa., Mar. 26, 1896.
- A. Kekulé, University of Bonn, Germany, July 13, 1896.
- Wilhelm Pickhardt, New York City, Sept., 1896.
- Alfred Mason, New York City, Nov. 2, 1896.
- H. A. Mott, Jr., New York City, Nov., 1896.
- Walton C. Tidball, Brooklyn, N. Y., Nov. 21, 1896.
- James C. Foye, Chicago, Ill., 1896.

The following gives in detail the changes in membership during the past year :

(5)

|                            | Members. | Associates. | Honorary members. | Total. |
|----------------------------|----------|-------------|-------------------|--------|
| <b>GAIN.</b>               |          |             |                   |        |
| Elected and qualified..... | 126      | 18          | .                 | 144    |
| <b>LOSS.</b>               |          |             |                   |        |
| By death.....              | 9        | 3           | 1                 | 13     |
| By resignation .....       | 24       | 5           | .                 | 29     |
| By non-payment of arrears  | 38       | 3           | .                 | 41     |
| Total loss.....            | 71       | 11          | 1                 | 83     |
| Net gain.....              | 55       | 7           | -1 (loss)         | 61     |
| <b>ENROLLMENT.</b>         |          |             |                   |        |
| December 26, 1895.....     | 884      | 58          | 8                 | 950    |
| December 26, 1896.....     | 939      | 65          | 7                 | 1011   |

If to these we add the number of persons elected during the year who have not yet qualified by the payment of dues—all elected since November first not being required to qualify until the first of January—the grand total would be 1064.

The Society has now nine local sections distributed as follows: Rhode Island, Cincinnati, New York, Washington, D. C., Lehigh Valley, New Orleans, Chicago, Nebraska, and North Carolina.

All of these but one have presented their annual report to the General Secretary, as required by the constitution. Their activity and interest in chemical work are readily seen from the character of these reports.

In closing the report of the General Secretary for 1896, we would call attention to the fact that the Society, this year for the first time in its history, has reached a membership of more than one thousand. When we compare this with what it was a few years ago, we may well feel a just pride and gratification at the result. But we must not be contented with the record of the past or the attainments of the present, if we would maintain for the Society that commanding influence to which we may reasonably aspire.

|  |           |           |
|--|-----------|-----------|
| FINANCIAL STATEMENT OF GENERAL SECRETARY, DEC. 24, 1896.                       |           |           |
| Dues received from December 15, 1895, to December 24, 1896,<br>inclusive ..... | \$4800.00 |           |
| Interest on bank deposits.....   | 8.03      |           |
| Exchange balances in favor of American Chemical Society.....                   | .22       |           |
| Total receipts .....   | \$4808.25 |           |
| Paid to Treasurer of American Chemical Society, as per<br>vouchers.....        | \$4230.00 |           |
| General Secretary's Commission .....   | 480.00    |           |
|  |           | \$4710.00 |
| Balance on deposit in bank Dec. 24, 1896...                                    | \$ 98.25  |           |

ALBERT C. HALE,  
General Secretary.

(6)

TREASURER'S REPORT FOR THE YEAR 1896.

*Receipts.*

|   |           |
|---|-----------|
| Balance on hand December 26, 1895.....  | \$ 999.08 |
| Net dues and interest received from the General Secretary .....               | 4230.00   |
| Cash received for subscription to Journals and sales of back<br>numbers ..... | 606.51    |
| Cash received for advertisements in Journal.....                              | 488.85    |
| Interest from Farmers' Loan & Trust Co.....                                   | 14.63     |
|   | <hr/>     |
|   | \$6339.07 |

*Disbursements.*

|  |           |
|--|-----------|
| For expenses of General Secretary's Office ..... | \$ 548.81 |
| " " " Editor's Office .....                      | 40.99     |
| " " " Treasurer's Office .....                   | 150.00    |
| " " " Librarian's Office .....                   | 123.61    |
| " " " Buffalo Meeting.....                       | 108.10    |
| " " " Cleveland Meeting.....                     | 44.60     |
| " " " General and Miscellaneous.....             | 37.76     |
| " Publication of Journal.....                    | 3821.86   |

Rebates to Local Sections as follows:

|                   |          |
|-------------------|----------|
| Rhode Island..... | \$ 66.67 |
| Nebraska .....    | 16.66    |
| New York .....    | 179.00   |
| Washington .....  | 126.66   |
| Cincinnati .....  | 56.66    |
|                   | <hr/>    |
|                   | 445.65   |

Balance on hand December 26, 1896; as follows :

|                                    |           |
|------------------------------------|-----------|
| In Farmers' Loan and Trust Co..... | \$496.18  |
| In Bank of Metropolis .....        | 504.81    |
| Checks and cash on hand .....      | 16.70     |
|                                    | <hr/>     |
|                                    | 1017.69   |
|                                    | <hr/>     |
|                                    | \$6339.07 |

No bills or claims presented up to date and audited, remain unpaid.  
Accounts examined and found correct.

A. H. SABIN,  
A. P. HALLOCK,  
DURAND WOODMAN,  
Finance Committee.  
CHAS. F. MCKENNA,  
Treasurer.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Engineer's Club, 10 W. 29th St., New

York City, Monday, October 26, 1896, President C. B. Dudley in the Chair. There were present Messrs. C. B. Dudley, Austin, Breneman, Chandler, Dodge, Hale, Hart, McKenna and McMurtrie.

The minutes of May 10, 1895, and December 6, 1895, were read and approved.

The treasurer made a statement regarding the financial condition of the Society, and showing a balance of over \$1,200 in the treasury.

An informal report on the condition and prospects of the library was made by Mr. Dodge, Librarian.

The following resolution was adopted :

*Resolved*, That the Finance Committee of the American Chemical Society is hereby authorized to approve, and the Treasurer to pay to the General Secretary each month during the year 1897 a bill or bills for clerical help; provided, however, that the total sum called for by said bills does not amount to \$250.

The President read some correspondence with A. A. Noyes, of Boston, in reference to the publication of abstracts of American Chemical Research in the Journal of the Society, and upon motion of Mr. McMurtrie, it was resolved that the President of the Society and the Chairman of the Committee on Papers and Publications be constituted a committee with power to conclude an arrangement with Dr. A. A. Noyes, for the publication of the "Review of American Chemical Research," in the current issues of the Journal of the American Chemical Society; said action, however, to be subject to the approval of the Council.

It was voted that the price of the Journal per year hereafter be \$5.00 to all persons without distinction.

It was voted also that the President of the Society, the Chairman of the Committee on Papers and Publications, and the Librarian be constituted a committee to arrange for such reprints of back numbers of the Journal as shall be necessary.

It was voted that the President of the Society shall appoint a committee of three Directors, of which he himself shall be Chairman, to make a contract for the future publication of the Journal, which contract shall be subject to the approval of the Council.

The action of the Editor, up to the present time and until January 1, 1897, in increasing the number of copies of the Journal to meet the probable demands for it, was approved.

The President announced that Dr. Charles F. Chandler had been added to the Committee on Advertising.

Upon motion, duly seconded, it was voted that the Chairman of this Board be authorized to appoint a committee of three Directors, of which the President of the Society shall be Chairman, to consider the question of the revision of the Constitution, and to report to the Board at its next meeting what they consider the wisest course to be taken in the matter.

Upon motion of Prof. Chandler, it was decided that when the Board adjourn, it be to meet at 51 East 54th St., New York City, Nov. 30, 1896, at 7 P. M.

The meeting then adjourned.

ALBERT C. HALE,  
Secretary.

President Dudley has appointed the following gentlemen to serve on the committees mentioned above.

On contract for future publication of the Journal—President Dudley, Chairman; H. W. Wiley, Wm. McMurtrie.

On advisability of revising the constitution—President Dudley, Chairman; C. F. Chandler, C. E. Munroe.

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The Board of Directors having arranged, through a committee consisting of the President and the Editor, for the publication in the Journal of a review of American Chemical Research, subject to the approval of the Council, this action has now been approved and the committee has accordingly executed the contract.

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#### COUNCIL.

The Council has directed that the dues for membership for 1897 be collected by the General Secretary as in the current year, and that he be allowed ten (10) per cent. on all collections as compensation for his work.

It was also ordered that the salary of the Editor for the year 1896 and for the year 1897 be fixed at \$250 per year.

#### NEW MEMBERS ELECTED NOVEMBER 16, 1896.

Alden, John, Lawrence, Mass.

Brakes, James, care Chateaugay Ore & Iron Co., Lyon Mountain, N. Y.

Cappon, Thomas Wm., 311 Manhattan Ave., Brooklyn, N. Y.

Dortch, F. W., Med. Dep't., Vanderbilt Univ., Nashville, Tenn.

Ferguson, George A., College of Pharmacy, West 67th St., N. Y.

Flynn, Oscar Rogers, 302 Hamlet St., Columbus, O.

Leach, Miss Mary F., Mount Holyoke College, South Hadley, Mass.

Lord, Prof. N. W., Ohio State University, Columbus, O.

Millwood, James P., 1694 Madison Ave., N. Y. City.

Neustadt, Geo. M. S., 151 E. 33rd St., N. Y. City.

Rossi, August J., 35 Broadway, N. Y. City.

Sill, Herbert F., Princeton Univ., Princeton, N. J.

Stocker, John H., Boys' High School, Brooklyn, N. Y.

Vinson, Albert E., N. E. corner Neil and Tenth Ave., Columbus, O.

**ASSOCIATE ELECTED NOVEMBER 16, 1896.**

Dunlap, Charles J., Princeton Univ., Princeton, N. J.

**NEW MEMBERS ELECTED DECEMBER 14, 1896.**

Alsop, Wm. K., 30 Ferry St., N. Y. City.

Arnold Fred. N., Jr., 14 Garfield Place, Cincinnati, O.

Bush, Charles S., 212 Weybosset St., Providence, R. I.

Chamberlin, W. E., 436 West Broadway, N. Y. City.

Eachus, Charles, 30 Ferry St., N. Y. City.

Hall, Prof. Vernon, Evanston, Ill.

Heileman, W. H., Agr. Exp. Station, Pullman, Wash.

MacCready, E. B., Durham, N. H.

Martin, Wm. J., Davidson, N. C.

May, George H., Newton Center, Mass.

Pope, Fred. J., School of Mining, Kingston, Ontario.

Schaffer, Herbert Allen, Easton, Pa.

Stillman, John Maxson, Stanford Univ., Cal.

**ASSOCIATE ELECTED DECEMBER 14, 1896.**

Jones, Arthur Owen, Highland Ave., Walnut Hills, Cincinnati, O.

**NEW MEMBERS ELECTED DECEMBER 24, 1896.**

Higbee, Dr. H. H., Hamilton College, Clinton, N. Y.

Hunter, J. R., Ph.D., Richmond College, Richmond, Va.

Marsters, John L., care of N. Y. & Pa. Co., Lock Haven, Pa.

Newberry, William Belknap, Easton, Pa.

Phillips, William B., Ph.D., Birmingham, Ala.

Pickel, J. M., Ph.D., Univ. of Alabama, Tuscaloosa, Ala.

Vulté, Hermann T., Columbia University, N. Y. City.

Woolworth, James G., 298 Fountain St., Providence, R. I.

## ASSOCIATES ELECTED DECEMBER 24, 1896.

Belden, Edgar Tweedy, Allentown, Pa.

Bender, Hermann Harry, 744 W. Court St., Cincinnati, O.

## CHANGES OF ADDRESS.

Adriance, John S., 321 Lexington Ave., N. Y. City.  
 Hall, Clarence A., Lake Superior Carbide Works, Sault Ste. Marie, Mich.  
 Hancock, David, 1720 Fifth Ave., Birmingham, Ala.  
 Hollick, Herbert, Syracuse, N. Y.  
 Hollinger, M. J., Star Furnace Co., Jackson, Jackson Co., O.  
 Kenan, Wm. R., Jr., Box 185, Wilmington, N. C.  
 Lenher, Victor, Mechanicsburg, Pa.  
 Potter, C. A., 161 Fountain St., Providence, R. I.  
 Richards, Edgar, 341 W. 88th St., N. Y. City.  
 Twitchell, Mayville W., 712 N St., N. W., Washington, D. C.

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## MEETINGS OF THE SECTIONS.

## WASHINGTON SECTION.

A regular meeting was held Thursday, November 12, 1896. The President, Dr. de Schweinitz, was in the chair, with fourteen members present. Mr. V. K. Chesnut, in the absence of the Secretary, acted as Secretary. The minutes of the preceding meeting were read and approved. A communication from the Medical Society of the District of Columbia was read, in which the Society was requested to appoint a member to serve as its representative in a Joint Commission on Vivisection, this commission to be charged with the duty of investigation relating to the practice of animal experimentation in the District of Columbia, and the representation of the constituent organizations (The Medical Society of the District of Columbia, Bureaus of Medicine and Surgery of the Army and Navy, Marine Hospital Service and Animal Industry, The Medical Departments of the Columbian, Georgetown, Howard, and National Universities and the Chemical, Biological, Anthropological, Entomological, and Philosophical Societies of the District of Columbia) before Congress in such manner as said commission may determine.

There being no further business the reading of papers was proceeded with. The first paper was by V. K. Chesnut on "Poisonous Honey."

The speaker gave an account of the literature, and enumerated

several recent cases of poisoning which happened in New Jersey and North Carolina. Reports of other poisonous honey have been received from Texas and California.

The principal cases were ascribed to honey derived from the laurels (*Kalmia latifolia* and *Kalmia angustifolia*). A new method of detecting the presence of andromedotoxin in honey was described. Specimens were exhibited of poisonous honey and the plants from which such honey was derived.

The discussion of Mr. Chesnut's paper was by Prof. Stokes, Munroe and Seaman and Dr. de Schweinitz. Prof. Stokes asked if the flower of the horse chestnut was known to be poisonous to bees. Mr. Chesnut was not aware of the fact, but thought it possible; the flowers of the Judas tree have a similar reputation. Prof. Munroe spoke of the honey locust, Prof. Seaman of the possible evaporation of gelsemine from gelsemium honey, and Dr. de Schweinitz cited a historical case of poisoning which happened in Asia Minor.

The second and last paper was by Dr. de Schweinitz, on "A Convenient Lamp for Generating Formaldehyde Gas and Acetic Aldehyde." The speaker exhibited several forms of lamps in working order, and explained the device. Ordinary lamps are used, but the upper part of the wick is supplemented by a piece of platinized asbestos. The cotton wick was turned high enough to light. After burning a minute or so the platinized asbestos began to glow and the flame was extinguished. The glow continues till all of the alcohol is exhausted. The decomposition is simple. With methyl alcohol, formaldehyde and water are the chief products; with ethyl alcohol, acetaldehyde and water.

Traces of carbonic, formic, and acetic acids are also present in the reaction. The discussion of Dr. de Schweinitz's paper was by Dr. Fireman. Dr. Fireman asked what the yield of aldehyde was. Dr. de Schweinitz replied that he did not have the exact figures at hand but that he obtained about three-fourths of the theoretical yield.

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A regular meeting of the Washington Section was held December 10, 1896, with the President, Dr. de Schweinitz in the chair. There were thirty members and several guests present. The minutes of the preceding meeting were read and approved.

Dr. Marcus Benjamin, of the Smithsonian Institution, already a member of the Americal Chemical Society, was elected to membership in the section.

The first paper of the evening was by Prof. H. W. Wiley on "The Mechanical Analysis of Phosphatic Slags."

The second paper was by Prof. Charles E. Munroe, entitled "An Early Specimen of Guncotton." Professor Munroe called attention to a sample of guncotton which he had received from Dr. W. A. Hedrick some two years ago, and which had been for many years in the possesion of Dr. B. S. Hedrick, formerly examiner in the U. S. Patent office. The specimen was in the form of a cartridge, consisting of long staple guncotton, and although the paper was torn somewhat it was still possible to read that it was labeled "Cotton for Shooting," and that it was made by "Lennig, of Philadelphia, under patent of October 6, 1846."

The guncotton is in a complete state of preservation, and as it apparently dates from shortly after Schoenbein's patent was filed, it is probably the oldest specimen in this country, and shows that properly made guncotton is a stable product. Prof. Munroe then offered in the same connection a copy of Schoenbein's original United States patent, and discussed his claim to being the original discoverer of guncotton, holding that although he had much improved the process of manufacture, and made it practicable, that others, among whom were Pelouze and Dumas, had preceded him in producing an explosive cellulose nitrate. There was some discussion especially as to a discrepancy between the dates of the patent and that on the specimen presented by Prof. Munroe. Dr. Woodridge, who was present as a guest, in response to an invitation from the President, stated that he had nothing to add to Prof. Munroe's remarks. Dr. W. S. Hedrick referred to the connection of his father with the Patent Office, and said that formerly the laboratory of the Agricultural Department, which was then under the Interior Department, was connected with the Patent Office, and he thought the specimen might have come from this laboratory. Dr. Littlewood said that he had tried to obtain further data, but had found no explosives in the office as old as this specimen. He further stated that few would be handed down by him to his successor, as his policy was to remove all explosives as soon as possible. He referred to the

fact that the last time he saw Maxim, the latter had just lost one arm as the result of some of his experiments with high explosives. The only specimen now in the Patent Office is a small specimen of Cordite kept in a glass. Mr. Dewey said that he would not put much faith in the data on the specimen. Lennig may have made a mistake in the data. He was sceptical as to its age. Prof. Munroe said that if it dated back only to 1860 it was old. After further discussion by Dr. Fireman and Prof. Munroe, Mr. W. D. Bigelow gave a description of a "Convenient Apparatus for the Estimation of Urea in Urine by the Hypobromite Method." The apparatus consisted of a burette so bent that the graduated part forms the arc of a circle, the center of which is a lip at the end farthest from the stopcock. Above the stopcock is a thistle-tube top for the introduction of the reagents. At 9.40 P. M. the meeting adjourned.

#### CINCINNATI SECTION.

The forty-seventh meeting of the Section was held in The Lloyd Library, Tuesday evening, December 22, 1896.

In a paper on "The Action of Fused Sodium Dioxide on Metals," Prof. W. L. Dudley gave an interesting account of an attempt to render iridosmine more easily soluble, and the consequent discovery of the action of sodium dioxide at high temperatures on gold, silver, nickel, and iron. Samples of crystalline substances formed as the result of this action were exhibited.

The annual election resulted as follows :

President—E. C. Wallace.

Vice-Presidents—Prof. W. L. Dudley and Prof. O. W. Martin.

Secretary—Dr. S. Waldbott.

Treasurer—Henry B. Foote.

Directors—Prof. F. Homburg, Prof. H. E. Newman, and Prof. Hannah L. Wessling.

Fred. N. Arnold and Arthur O. Jones, of Cincinnati, and Prof. Carrie E. Joslin, of Terre Haute, Ind., were elected members of the Section.

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#### NEBRASKA SECTION.

In the absence of the president, Dr. White was elected tem-

porary chairman, and called the meeting to order December 18, 1896.

On motion of Miss Bouton, the following were elected to membership in the Section : F. C. Cooley, F. S. Culver, Burton Dales, Mary Fossler, G. W. Heinrod, M. E. Hitner, Helen P. Langer, Eva O'Sullivan, H. C. Parmelee, and R. W. Thatcher.

Upon motion of Dr. Avery, the chair appointed a committee consisting of Dr. Avery, Mr. Elliott, and Mr. Tucker, for the purpose of soliciting subscriptions from the members of the Section to the Lavoisier Monument Fund.

The paper of the evening was read by P. L. Hibbard, of the Argo Manufacturing Co., of Nebraska City, entitled, "The Manufacture of Starch and Chemistry as Applied Therein," in which he described in detail the methods of separating, washing, purifying, and drying starch, and spoke of the various chemical methods for testing the purity, the amount of waste, and the quality of the manufactured starch. The paper gave rise to much discussion, since the chemical methods appear to be very inadequate.

The meeting then adjourned.

Issued with February Number, 1897.

## Proceedings.

### COUNCIL.

The following persons have been elected as members of the Standing Committees for 1897:

*Committee on Papers and Publications* : J. H. Long, Thomas B. Osborne.

*Committee on Nominations to Membership* : A. A. Breneman, P. T. Austen, C. A. Doremus.

*Finance Committee* : Durand Woodman, A. P. Hallock, A. H. Sabin.

### BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the residence of Dr. Charles F. Chandler, 51 East 54th Street, New York City, Thursday, Nov. 30, 1896.

After dinner, which was served at 7:30 p. m., the meeting was called to order for business by President Dudley.

The minutes of the last meeting of the Board were read and approved.

President Dudley, on behalf of the committee to make arrangements with Dr. A. A. Noyes for publishing the "Review of American Chemical Research" in the Journal of the Society, reported, and asked for further instructions. The board instructed the committee to conclude arrangements with Dr. Noyes in accordance with its own discretion.

A report of the committee on the advisability of revising the constitution was then made, and its recommendations discussed, after which the board ordered the recommendations transmitted to the committee of the council appointed for the purpose of considering such suggestions.

The board then adjourned.<sup>1</sup>

ALBERT C. HALE, Sec.

<sup>1</sup> NOTE BY THE EDITOR.—Minutes of this meeting should have been published last month but were not received from the Secretary in time to allow of it.

## MEMBERS ELECTED JANUARY 22, 1897.

Appleton, H. A., F.C.S., 2 Glenholme Terrace, Borough Road, Middlesbrough-on-Tees, Yorkshire, Eng.  
 Bevier, Miss Isabel, Penna. College, Pittsburgh, Pa.  
 Bush, W. E., Rose Poly. Inst., Terre Haute, Ind.  
 Craver, H. W., Leechburg, Pa.  
 Daggett, W. W., Pulaski City, Va.  
 Foster, Wm., Jr., Princeton Univ., Princeton, N. J.  
 Gallup, Miss Harriet T., Kodak Park, Rochester, N. Y.  
 Hardin, Dr. W. D., John Harrison Lab., Univ. of Pa., Phila.  
 Harold, Joseph F. X., 636 Spruce St., Philadelphia.  
 Hero, Miss Ann, Vassar College, Poughkeepsie, N. Y.  
 Joslin, Prof. Carrie E., Coates College, Terre Haute, Ind.  
 Labonde, Dr. Leon, 171 Grand St., Brooklyn, N. Y.  
 Miller, Harry East, 1264 14th St., Oakland, Cal.  
 Oberholtzer, Dr. Vickers, Univ. of Pa., Philadelphia.  
 Smith, Frank Warren, Pinole, Contra Costa Co., Cal.  
 Smith, Warren R., Lewis Institute, Chicago, Ill.  
 Taggart, Walter T., 2011 Fairmount Ave., Philadelphia.  
 Werk, Louis, Westwood, Cincinnati, O.  
 Wing, Herbert H., care of R. Dunbar & Son, Buffalo, N. Y.

## ASSOCIATES ELECTED JANUARY 22, 1897.

Bunker, Henry A., 158 Sixth Ave., Brooklyn, N. Y.  
 Fuller, R. C., Fuller Iron Works, Providence, R. I.  
 Leavens, George D., Brooklyn Heights, N. Y.

## CHANGES OF ADDRESS.

Chapman, D. W., 352 E. 23d St., Chicago, Ill.  
 Sims, Clough W., 20 Morris Hall, Ithaca, N. Y.  
 Smith, Albert L., Box 163, Station O, Chicago, Ill.  
 Trubek, M., 77 E. 4th St., N. Y. City.

## MEETINGS OF THE SECTIONS.

## WASHINGTON SECTION.

The ninety-second meeting of the Washington Section was held January 14, 1897.

At this, the thirteenth annual meeting of the Society, the following officers were elected for the ensuing year; *viz.*:

*President*: W. D. Bigelow.

*Vice-Presidents*: H. N. Stokes, Peter Fireman.

*Secretary*: V. K. Chesnut.

*Treasurer*: W. P. Cutter.

*Executive Committee*: The foregoing officers and E. A.

de Schweinitz, Chas. E. Munroe, W. H. Krug, Wirt Tassin.

The annual address of the retiring president, Dr. E. A. de Schweinitz, was announced for February 25, the subject to be "The War with the Microbe."

NEW YORK SECTION.

The meeting was called to order in the rooms of the Knickerbocker Club, 45th Street and Madison Ave., at 8:20 P. M., with Dr. Wm. McMurtrie in the chair.

The following papers were read:

"Note on an Improved Specific Gravity Bottle for Liquids." By Dr. E. R. Squibb.

"Note on the Determination of Caffeine." By G. L. Spencer.

"Variations in the Composition of Commercial Red Lead." By Durand Woodman.

"Methods for Determination of Tannins." By J. H. Yocom.

"Modern Metallurgy of Copper." By J. B. F. Herreshoff.

Dr. Doremus moved that the Secretary be directed to convey the thanks of the Section to Dr. Henry Morton and to Dr. A. R. Leeds for the courtesies and generous hospitalities extended to the members on the occasion of the last meeting, held at the Stevens Institute of Technology. The motion was seconded and carried unanimously.

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The February meeting was held on the 5th at the College of the City of New York. Called to order at 8:30 P. M. Dr. Wm. McMurtrie in the chair, and about fifty members present.

The first hour was occupied in the "Discussion of the Relations of the Section with the Scientific Alliance and the Advisability of Severing those Relations."

Prof. Breneman opened the discussion.

Dr. Wiley described the work done by the affiliated Societies of Washington, and the advantages resulting from cooperation. He said that in the case of Washington they were all strictly professional societies with possibly one exception.

Dr. Austen thought the meetings were better attended when a special notice was sent out than when announced by the *Alliance Bulletin* only.

Prof. Breneman thought that the project for obtaining a build-

ing for the libraries and meetings of the allied Societies had not made the progress expected, if indeed it had made any progress.

Prof. Britton in reply said that the Council ultimately hoped to procure such a building, and that its efforts in this direction have met with considerable encouragement from several sources.

A motion to refer the question of severing the relations of the Chemical Society with the Alliance to the Executive Committee, was tabled.

Dr. H. W. Wiley read a paper on the "Value of Foods and the Methods of Ascertaining It," bringing out the disparity, until very recently, in the amount of interest and investigation devoted to "man foods" as compared with animal foods. He described the classes of foods rated according to their fuel values, according to their digestibility, etc., and pointed out the divergence between price and actual food value of many articles.

The papers on "Volumetric Estimation of Lead," by J. H. Wainwright, and "Electrolytic Production of Alkali Nitrites" by Wm. M. Grosvenor, were held over for the next meeting.

#### CINCINNATI SECTION.

The January meeting was held on January 15 this being the inaugural meeting held in the Chemical Lecture Room of the new Chemical Laboratory in Hanna Hall, University Buildings, with President E. C. Wallacé, later Prof. T. H. Norton, in the chair.

A paper of considerable local interest was read by John W. Hill, C.E., on "The Hygiene of Water." The speaker devoted himself mainly to the sanitary aspect of municipal water supply. He recalled the extensive investigations that have been made in this direction both in this country and abroad, and briefly touched upon the merits of sand filtration. The speaker strongly favors the theory borne out by certain evidence, that in the case of typhoid epidemics; water is the carrier of typhoid bacilli and of ptomaines generated thereby.

In the discussion which followed, Dr. S. P. Kramer urgently recommends prophylactic measures; *viz.*, to keep the rivers clean, especially free from sewage. Mr. Hill finally believes that with due regard to local conditions, the system of sedimentation and subsequent filtration of the Ohio river water would be the most feasible method of procuring an adequate supply of pure water.

**Issued with March Number, 1897.**

## **Proceedings.**

### **COUNCIL.**

By-Law No. 5, requiring members to be dropped from the roll if in arrears for one year has been amended so as to read "*if in arrears for two years.*"

The bills for printing the December number of the Journal amounting to \$344.45, were approved.

#### **NEW MEMBERS ELECTED MARCH 1, 1897.**

Bower, Wm. H., 29th St. and Grays Ferry Road, Philadelphia.  
Harrington, Edward M., Aetna, Lake Co., Ind.  
Haywood, John K., Div. of Chem., Dept. of Agr., Washington, D. C.  
Hewson, James H., 872 Broad St., Newark, N. J.  
Jones, A. B., P. R. R. Lab., Altoona, Pa.  
Keiser, Benjamin C., 99th St. and Torrence Ave., Chicago, Ill.  
Lenox, Prof. L. R., Stanford Univ., Cal.  
MacPherran, R. S., care of E. P. Allis Co., Milwaukee, Wis.  
Mittenzwey, Otto, care of Fitzgerald Bros., Troy, N. Y.  
Oberholser, R. L., Chester, Pa.  
Rowland, William L., 4800 Chester Ave., Philadelphia.  
Snoot, Lewis E., Alexandria, Va.  
Van Cleve, Carl E., 601 5th St. S. E., Minneapolis, Minn.  
Weed, Henry T., 298 Herkimer St., Brooklyn, N. Y.  
Winton, A. L., 136 Canner St., New Haven, Conn.

#### **ASSOCIATES ELECTED MARCH 1, 1897.**

Alexander, Jerome, 39 E. 60th St., N. Y. City.  
Anderson, Chas. A., 2421 Dearborn St., Chicago, Ill.  
Armstrong, Theodore, care of The Penna. Salt Mfg. Co.,  
Philadelphia.  
Baker, Miss Dicia H., 640 W. 7th St., Cincinnati, O.  
Chittenden, Horace W., 2421 Dearborn St., Chicago, Ill.  
Goessmann, Chas. I., Amherst, Mass.  
Hill, H. C., 36 Glenn Bldg., Cincinnati, O.  
Kunze, Wm. F., State Univ., Minneapolis, Minn.

Leenheer, Cornelius A., 2421 Dearborn St., Chicago, Ill.  
 Ott, Allen C., 2421 Dearborn St., Chicago, Ill.  
 Ryder, Louis W., 2421 Dearborn St., Chicago, Ill.  
 Smedes, Rev. Bennett, Raleigh, N. C.  
 Woolner, Arthur B., 2421 Dearborn St., Chicago, Ill.  
 Woolsey, Jesse F., 2421 Dearborn St., Chicago, Ill.  
 Wright, Frank, 2421 Dearborn St., Chicago, Ill.

#### CHANGES OF ADDRESS.

Barton, Edward, Univ. of Kansas, Lawrence, Kan.  
 Forrest, C. N., Chemist Long Island R. R., Long Island City, N. Y.  
 Williams, Chas. B., Johns Hopkins Univ., Baltimore, Md.

#### MEETINGS OF THE SECTIONS.

##### RHODE ISLAND SECTION.

A regular meeting of the Rhode Island Section was held at Providence on Thursday evening, December 17, 1896. After dinner at the Hope Club, the Section adjourned to the laboratory of Dr. H. C. Bumpus at Rhode Island Hall, Brown University. Dr. Bumpus gave a very interesting talk upon Practical Demonstration of the X-rays. The X-rays were produced and many objects were examined by aid of the fluorescope. During the evening photographs of the hand were made.

A meeting of the Rhode Island Section was held on the evening of Jan. 21, 1897. Chairman E. D. Pearce, presiding. Mr. Pearce described and illustrated with the aid of the microscope, crystals found in the pollen of various flowers. Mr. C. A. Catlin had prepared a few slides of the common starches which were examined under the microscope by the members present. Mr. W. M. Saunders described a method for determining formic aldehyde with standard ammonium hydroxide solution.

##### CINCINNATI SECTION.

The February meeting was held on February 16, 1897, in the Chemical Lecture Room of Hanna Hall, new University Buildings. President E. C. Wallace in the chair. Upon motion of Mr. Wallace it was decided that a question box be tentatively introduced at the meetings. A paper "Upon the Hydrolysis of Sulphonic Acids," was read by R. W. Proctor. Prof. Norton then gave a description of the details of the new laboratories, which were inspected after adjournment.

Issued with April Number, 1897.

## Proceedings.

### COUNCIL.

The bills for printing the January number of the Journal, amounting to \$414.53, are approved by Council.

Edward Hart has been elected editor for the year 1897.

### NEW MEMBERS ELECTED MARCH 29, 1897.

Bisbee, D. H., Dept. of Health, Chicago, Ill.

Freas, Thomas B., Hiawatha, Kansas.

Gooch, Prof. Geo. W., Chaffey College, Ontario, Cal.

Harms, Armin, P. O. box 28, Milwaukee, Wis.

Huntington, Dr. Harwood, 159 Front St., N. Y. City.

Hurlburt, E. B., Roxbury, Conn.

Hyde, Henry St. J., 210 E. 18th St., N. Y. City.

Kresge, Robert E., 428 Birch St., South Bethlehem, Pa.

Kuhns, Edwin J., The Bethlehem Iron Co., South Bethlehem, Pa.

Marshall, Prof. John, Univ. of Pa., Philadelphia.

McCaffery, Richard S., care of The Backus & Johnston Co., Lima, Peru, S. A.

Michaelis, Theodore, Western Sugar Refinery, Potrero, San Francisco, Cal.

Takamine, Jokichi, 6641 Woodlawn Ave., Chicago, Ill.

### ASSOCIATES ELECTED MARCH 29, 1897.

Finke, Alfred H., 9th and Race Sts., Cincinnati, O.

Germer, J. W., 2421 Dearborn St., Chicago, Ill.

Turnquist, C. M., 2421 Dearborn St., Chicago, Ill.

### CHANGES OF ADDRESS.

Carnell, Wm. C., care of Nelson, Morris & Co., U. S. Yards, Chicago, Ill.

Calkin, Wm. S., Spring Forge, Pa.

Colby, Dr. Albert Ladd, Bethlehem Iron Co., South Bethlehem, Pa.

DeChalmot, G., Holcomb's Rock, Bedford Co., Va.

Eberman, W. S., Capitol Building, St. Paul, Minn.

Eichberg, Dr. Julius H., 18 E. 9th St., Cincinnati, O.

Fosdick, E. H., care of Cal. Powder Works, Pinole, Cal.

Hancock, David, care of Woodward Iron Co., Woodward, Ala.

Hayes-Campbell, J., 446 E. 6th St., Newport, Ky.  
 Homberg, Prof. Fred., 104 W. Clifton Ave., Cincinnati, O.  
 Hurty, J. N., 102 N. Pennsylvania Ave., Indianapolis, Ind.  
 Kramer, Dr. S. P., 111 E. 9th St., Cincinnati, O.  
 Laudig, O. O., care of Monongahela Furnaces, McKeesport,  
 Pa.  
 Lewis, Gerald, Milford, Pike Co., Pa.  
 Ludlow, Gabriel, 95 Bayard St., New Brunswick, N. J.  
 Newman, H. E., 1370 Myrtle Ave., Walnut Hills, Cincinnati,  
 Ohio.  
 Ogilvy, D. J., 1403 State Ave., Cincinnati, O.  
 Parker, Charles E., 115 Park St., E. Orange, N. J.  
 Schiller, Louis J., care of Arbuckle Bros., Jay and John Sts.,  
 Brooklyn, N. Y.  
 Schmidt, Louis, 215 E. 4th St., Cincinnati, O.  
 Sicker, Fred. A., 524 Bloomfield St., Hoboken, N. J.  
 Twitchell, E., 2644 Bellevue Ave., Mt. Auburn, Cincinnati,  
 Ohio.

#### MEETINGS OF THE SECTIONS.

##### NORTH CAROLINA SECTION.

The second annual meeting of the North Carolina Section of the American Chemical Society was held in the offices of the North Carolina Experiment Station, February 22, 1897, at 4 o'clock, with Prof. F. P. Venable in the chair and twelve members and four visitors present. Messrs. A. W. Belden and A. W. Blair were elected members. The Section now has twenty-two members. The following papers were read:

Chairman Venable's annual address : The Present Position of the Periodic System.

Instruments for the Graduation and Calibration of Volumetric Apparatus. By B. W. Kilgore.

Silicon Alloys with the Metals. By G. deChalmot.

Unit of Volume. By B. W. Kilgore.

Officers for the ensuing year were elected as follows : Chairman, F. P. Venable; Vice-Chairman, C. E. Brewer; Secretary and Treasurer, B. W. Kilgore.

The meeting then adjourned to come together at the call of the Executive Committee.

##### RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence on Thursday evening, February 25, 1897, Chairman E. D. Pearce, presiding. Mr. R. C. Fuller read a paper upon "Ele-

ments of Making Lantern Slides." The paper was illustrated by means of the stereopticon. Over 100 views were shown emphasizing the points made by the reader.

#### WASHINGTON SECTION.

The ninety-third regular meeting of the Chemical Society of Washington was held in Sängerbund Hall, Washington, D. C., February 11, 1897. The Society was called to order at 8 P. M. by the president, Dr. Bigelow, with twenty-five members, and several invited guests present.

Mr. G. E. Patrick applied for membership and, being already a member of the American Chemical Society, was duly elected as a member of the local section.

Under the head of new business, communications were read from the Biological and Geological Societies of Washington, replying favorably to the request of this Society in the matter of sending their programs to members requesting them.

The first paper of the evening was read by Dr. E. W. Allen, and was entitled "A Critical Review of Aikmann and Wright's Translation of Fleischmann's *Lehrbuch der Milchwirtschaft*," an abstract of which has been presented by the author. Attention was called to the heavy, verbose style of the translation, and often foggy statements, errors in translating the sense, and failure to adapt the book for English and American readers, and to correct certain statements which do not apply in the present status of knowledge. The fallacy of translating a book for students and semi-popular use, without editing the translation, and in a measure adapting it to the new field, was pointed out.

Dr. H. Carrington Bolton exhibited two British patents issued in 1884 and 1889; one being a process for "getting gold from wheat" by merely cutting the wheat straw into "snips," steeping them in "water at 59° Fah., varying with the temperature," and skimming off the gold with a cylinder of "some cool substance as china or earthenware."

The second patent is for an apparatus to be used in divining the presence of precious metals underground, issued to a Texas farmer. It consists of a sealed bottle, filled with several metals and either nitric acid, tartaric acid or alcohol, held by a string.

Mr. W. H. Krug read a review from the German, of a paper

by Adolph Meyer, entitled "The Maximum of Plant Production."

Mr. Wirt Tassin's paper was entitled "A New Blowpipe Reagent," and he presents the following abstract:

"The speaker gave a review of the use of iodine in blowpipe analysis from the time of Bunsen to Haanel and Andrews. He then stated that for several years past he had been using iodine in several forms, and found that a mixture of equal parts of iodine and potassium thiocyanate plus a little sulphur, the whole being intimately mixed, fused, and then ground, gave the most satisfactory results. The powder was used as a flux on a gypsum tablet.

A series of the iodide and cyanate films produced by some forty minerals was shown. Some of these illustrated the extreme delicacy of the test; others showed the effect that the coating produced by one element had upon that produced by another when they were deposited together; still others showed the methods of differentiating interfering elements. Some attempts at quantitative methods were shown; and attention was called to the fact that a mixture of three parts of alcohol and one part of chloroform burned in a lamp gave rise to some very interesting reactions, either with or without the iodine flux."

The Society adjourned at an early hour and the remainder of the evening was devoted to feasting and to social intercourse.

A special meeting of the Chemical Society was held Tuesday, March 9, 1897, in the Assembly Hall of the Builder's Exchange Club, under the auspices of the joint commission of the Scientific Societies of Washington, to hear the address of the retiring president, Dr. E. A. deSchweinitz, upon "The War with the Microbes." The speaker was introduced by Surgeon-General Sternberg of the U. S. Army. The hall was filled with members of the Society, medical men, and over 300 invited guests from the other Scientific Societies of Washington.

#### CINCINNATI SECTION.

The March meeting of the Section was held on March 16th in the Chemical Lecture Room, Hanna Hall, University Buildings, Mr. Henry B. Foote chairman by nomination. Miss Dicia H.

Baker, of Cincinnati, and Mr. Louis Werk, of Westwood, O., were elected members of the Section.

Miss Hannah L. Wessling read a paper on "Lavoisier," giving a review of the life and work of the unfortunate French chemist. Mr. Frank N. Smalley then read a paper on "The Halogen Derivatives of the Methylamines."

#### NEW YORK SECTION.

The regular monthly meeting was held at the College of the City of New York on Friday evening, March 5, Dr. Wm. McMurtrie presiding.

The following papers were read:

Volumetric Determination of Lead. By J. H. Wainwright.

Determination of Lead in Lead Ores. By Richard K. Meade.

Electrolytic Production of Alkali Nitrites. By Wm. M. Grosvenor.

Method of Drying Sensitive Organic Substances. By C. C. Parsons.

Chemistry of the Sanitary Control of City Milk Supplies. By E. J. Lederle.

Quantitative Separations by Sodium Nitrite. By Gillett Wynkoop.

Composition of Beet Sugar Ash. By C. F. A. Meisel.

The relations of the Section to the Scientific Alliance were discussed and the matter referred to the Executive Committee, and a special committee of four to be appointed by the chair.

The coming annual exhibition of the Academy of Sciences at the Museum of Natural History was announced by Dr. C. A. Doremus, and members of the Chemical Society were urged to bring forward any new and original work of interest. The meeting was then adjourned.

#### NEBRASKA SECTION.

The meeting was held in the Chemical Laboratory of the University of Nebraska, on Friday, March 19. In the absence of the president, the secretary, Dr. John White, called the meeting to order and was elected chairman *pro tem.*

Dr. Avery, on behalf of the committee appointed to collect a subscription to the Lavoisier Monument Fund, reported progress, stating that a total of eight dollars had been subscribed. This was ordered turned over to the treasurer for forwarding to the Monument Committee.

Mr. R. S. Hiltner read an exceedingly interesting paper upon the composition of ciders. This was a report of progress upon work

being carried on in the Experiment Station laboratory and will be published in due form upon completion. The chemical methods used aroused considerable discussion.

Mr. Benton Dales described a new electrolytic method for the determination of cadmium. In brief, the method consists of the precipitation electrolytically from a double formate solution, and, when certain conditions are complied with, as governing the strength of solution, the preservation of a proper ratio between the amount of cadmium contained and the plating surface and the regulation of the current, the results are all that could be desired.

Dr. H. A. Senter, who has recently returned to the University after taking a degree in Germany, entertained the Section very pleasantly by giving an instructive as well as entertaining account of his visits, as a member of a class in technical chemistry, to various manufacturing establishments in Germany, such as gas works, breweries, color factories, distilleries, beet sugar factories, Portland cement works, and various others. He stated that the proprietors of the German factories are very suspicious of foreigners, and for that reason it is difficult to get any detailed information upon the chemical processes employed.

**Issued with May Number, 1897.**

## **Proceedings.**

### **COUNCIL.**

Professor W. A. Noyes, Terre Haute, Ind., has been elected a member of the Council to fill the vacancy caused by the resignation of J. H. Appleton.

A majority of the Council have voted for Detroit as the place for the summer meeting, to be held August 9 and 10, 1897.

### **NEW MEMBERS ELECTED APRIL 9, 1897.**

Allen, H. H., Patent Office, Washington, D. C.  
Beal, W. H., Dept. of Agr., Washington, D. C.  
Griffin, J. H., Patent Office, Washington, D. C.  
Noyes, E. R., Museum of Hygiene, Washington, D. C.  
Thorp, Frank H., Ph.D., Mass. Inst. Tech., Boston, Mass.

### **CHANGES OF ADDRESS.**

Behr, Arno, 5501 Cornell Ave., Chicago, Ill.  
Blair, A. W., Guilford College, N. C.  
Carman, J. S., Bothwell, Ontario.  
Case, W. A., 23 Chestnut Ave., Baltimore, Md.  
Frohman, E. D., Care of O. Hommel & Co., 23d St. and Penna. Ave., Pittsburg, Pa.  
Graham, W. H., care of H. Maxim, Esq., 337 Norwood Road, London, S. E., England.  
Hazen, Allen, 220 Broadway, New York City.  
Hunsicker, Geo. W., 141 North St., Allentown, Pa.  
LaWall, Chas. H., 301 Cherry St., Philadelphia, Pa.  
Little, A. D., 7 Exchange Place, Boston, Mass.  
Mar, F. W., Richmond Hill, L. I., N. Y.  
McMurtrie, William, 100 William St., New York City.  
Roeser, Frederick, care of Oceana Consolidated Co., Ltd., Johannesburg, South African Republic, Africa, Box 1542.  
Schüppelhaus, Robert C., care of Geo. H. Graham, 66 Broadway, New York City.  
Wade, E. H., 115½ N. Main St., Los Angeles, Cal.  
Williams, John T., Stamford, Conn.  
Wrampelmeier, T. J., 120 Lyon St., San Francisco, Cal.

## ADDRESSES WANTED.

Flowers, J., formerly of Agricultural Experiment Station, Bozeman, Mont.

Shaw, Wm. T., formerly of Agricultural Experiment Station, Bozeman, Mont.

## MEETINGS OF THE SECTIONS.

## WASHINGTON SECTION.

The ninety-fourth regular meeting of the Chemical Society of Washington was called to order at 8 P.M., in the Cosmos Club Hall, March 11, 1897, by the president, Dr. Bigelow, with twenty-one members present. Mr. J. Dabney was elected to associate membership.

The first paper of the evening, "Some Theories of Crystal Structure," was read by Wirt Tassin, who presents the following abstract: "The hypotheses of Bravais, Lireing, and Sohncke were reviewed. A synopsis of the methods by means of which these investigators arrived at their conclusions, together with examples of the several kinds of 'space lattices' were given. Attention was called to the fact that as early as 1830 Hessel had demonstrated that only thirty-two types of symmetry were possible in a homogeneous figure under conditions agreeing with the law of rational indices: and that the theories of Bravais, Sohncke, and others failed to include these thirty-two types, and no more, unless they supposed, that in their molecular arrangements, the molecules themselves possessed various shapes, or that the crystal structure consisted of different kinds of particles.

"The author then took up the more recent structural theory of Federow and Schonflies which requires only that the structure of the crystal consist of similar molecules, and allows the chemist and the physicist to decide the character of these molecules. It was pointed out that the essential difference between the Sohnckian hypothesis and that of Schonflies was that Sohncke requires that in a system of points, which is to have the characters required by a crystal structure, around every point the arrangement of the remainder is the same as around every other point," and all of his structures are derived by moving one point to another by sliding, rotating, and screw motions. Schonflies, on the other hand, defines a crystal as "consisting of absolutely

similar molecules, so arranged that each molecule is environed in the same way by all the other molecules" as that one part of the system may be derived from the other by reflection. Mention was made of Barlow's work and examples given and the paper closed with a list of those predictions of new compounds which have been verified and which were based upon theories treating of the relations between form, structure, and composition."

As a supplement to Mr. Tassin's paper, Dr. F. K. Cameron read a short resumé of "The Effect of Substitution on Isomorphism and Crystal Structure in Organic Compounds." The brilliant uses made of the principles of isomorphism in inorganic chemistry led to its introduction by Laurent, Pasteur, and others into the study of organic compounds. The importance of isognomism was however too greatly accentuated in comparison with the identity of crystal system which came to be regarded as of but accidental importance. Kopp ridiculed these ideas but they have since been advanced by Groth.

"The relationships thus far brought out are: Substitution may cause the system to increase or diminish in symmetry, or may cause the lengthening or shortening of axes.

"With the substitution of one or a few atoms by other atoms or groups, the system generally changes and to one of less symmetry; if all or nearly all the equivalent atoms or groups are replaced alike, the derivative generally regains the symmetry of the original substance. But the change is greatly dependent upon the nature of substance itself, the orientation of the substituting agent, and the nature of this agent.

"In molecules of great complexity the changes are generally much less than in simpler molecules. In molecules of great complexity (that is, in organic compounds, and assuming the tetrahedral structure of the carbon atom) the crystal will probably have the same symmetry as the molecule.

"These relations are all entirely empirical. The only suggestion of any importance so far put forward is that of Groth, that in substances showing morphotropic relationship, it is to be assumed that the crystal nuclei, or physical molecules, are of the same order of magnitude. This accounts for the fact that substances with the same percentage composition may vary so

greatly in their properties, but is fatally weak in that it does not in any way necessitate the existence of morphotropic relationships."

The effect on crystal structure was illustrated by a comparison of the benzol and of the ammonium platinichloride compounds. Neither OH nor NO<sub>2</sub> seem to have much morphotropic value. Repeated substitution in the platinichlorides often restores the symmetry of the mother substance but the substitution of ethyl brings about a complete change.

The second paper presented by W. H. Krug and J. E. Blomén, was entitled "A Recalculation of Wein's Table of Starch Equivalent to Copper Found Based on the Factor 0.92."

"Starch or dextrine can be directly obtained from the copper found by converting the starch into dextrine and determining the latter with Allihn's solution. This table is based on the factor 0.90 which assumes that the formula of starch is (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, and that it is all converted into dextrose. Nägeli determined the formula of starch to be C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, and if this be correct the factor becomes 0.918. Ost working with the Sacchse method decided upon the factor 0.925. In view of all these conflicting data, Wiley recommends the factor 0.92, a mean between the two last cited, which will give the analyst fairly accurate results. This factor was used in the recalculation of the table."

The last paper was entitled "Malt Wine" and was read by Dr. D. J. Kelly, who presents the following abstract:

"He pointed out how Ordonneau, Jacquemin, Tettelin, Rommier and Sauer recognized the profound changes produced in the fermentation of a sweet liquid according to the kind of ferment employed. They found that when the juice of a poorer variety of grape was fermented by the aid of the ferment peculiar to a choicer kind, it became a wine having many of the characteristic properties of the better kind; a solution of sugar and water, to which appropriate yeast food and then wine ferment was added, was fermented and submitted to distillation; the result resembled brandy. When ordinary malt wort is sterilized, and then instead of being fermented with the usual *saccharomyces cerevisiae* or brewer's yeast is fermented with the *saccheromyces ellipsoideus*, or fruit yeast, the resulting liquid resembles a fruit wine, and the liquid distilled therefrom a

brandy. In his recently patented process Sauer ferments a sterilized malt-wort by a pure culture of a ferment derived from the bloom of the cherry or the Tokay grape, modifying the old process in certain important details, and obtains wines, specimens of which were submitted to the audience, and pronounced to be scarcely distinguishable, if at all, from the genuine articles." Dr. Kelly suggested that possibly the substitution of a properly selected grape or other wine yeast for that now employed in the process of bread making, might be found to modify very agreeably this article of daily consumption.

In the discussion of this paper Dr. Bigelow called attention to the complications which would arise in the food laws upon the introduction of this beverage and questioned whether it should properly be called wine. Dr. Ely thought that it should be taxed as beer. Prof. Seaman spoke of the rôle played by the esters in wines and of synthetic foods in general, claiming that malt wine was as much a real wine as synthetic sugar was real sugar. The popular prejudice against the use of synthetic foods would be greatly lessened by furthering the study of chemistry among the masses of the people. Dr. deSchweinitz stated that in regard to butter substitutes, the objection was sometimes due to the unsanitary conditions of the place of manufacture.

The meeting adjourned at 10.10 P. M.

V. K. CHESNUT.

#### LEHIGH VALLEY SECTION.

A meeting was held at Easton in the Chemical Laboratory of Lafayette College, on April 1. Dr. Colby, presiding officer, occupied the chair. The following officers were elected for the ensuing year: President, Jos. W. Richards; Secretary and Treasurer, Bernard Enright; Executive Committee: Albert Ladd Colby, Porter W. Shimer, Jos. W. Richards, and Bernard Enright. A resolution of thanks was passed in appreciation of the efficient services of the retiring presiding officer, Albert Ladd Holby, and the retiring secretary and treasurer, Albert H. Welles. Wm. Newberry, of Easton, was elected a member of the Section. The subject chosen for topical discussion at the next meeting is "The Effect of Silicon in Pig Iron and in Iron Castings."

BERNARD ENRIGHT.

## CINCINNATI SECTION.

The April meeting was held on April 15 in the Chemical Lecture Room of Hanna Hall, University buildings, Prof. O. W. Martin in the chair. Mr. J. Henry Schroeder read a paper "On Some Recent Progress in the Study of the Tannins." The demonstration of a number of specimens of different tannins, forwarded upon request for the occasion by Prof. Trimble, of Philadelphia, lent additional interest to the paper.

The discussion which followed brought out some notable points. Mr. Westenfelder stated that the diminution in the percentage of nitrogen in the hides measures to some extent the progress of the tanning process, which he thinks is a chemical rather than a physical phenomenon.

As regards the hide powder process for estimating tannin, Dr. Hurty, of Indianapolis, says that in his experience it does not give uniform results, and points out that beside tannin there are other substances, *e.g.*, bitter principles and coloring matters, which have tanning properties; hence the tanning value of a bark, etc., should not be judged solely by the amount of tannin it contains.

Prof. Norton incidentally called attention to the curious fact that tannin was probably the first organic reagent known in antiquity.

Prof. Norton then introduced for discussion the subject "The Nomenclature of Alkaloidal Salts," with a view of aiding the movement now on foot to do away with the discrepancies existing in that direction in the language of chemistry, pharmacy, and trade.

On motion the meeting adjourned.

S. WALDBOTT.

Issued with June Number, 1897.

## Proceedings.

### COUNCIL.

The following report from the Committee on Duty-Free Importations has been received, the recommendations adopted, and the report ordered printed in the Proceedings:

THE COLUMBIAN UNIVERSITY, WASHINGTON, D. C.

CORCORAN SCIENTIFIC SCHOOL, APRIL 22, 1897.

*Dr. C. B. Dudley, President of the American Chemical Society :*

*Sir* : Your Committee on Duty-Free Importations have considered the present state of tariff legislation and find that H. R. Bill 379 of the Fifty-fifth Congress, first session, (commonly known as the "Dingley Bill,") as presented to the Senate, contains the following :

" Sec. 629. Scientific apparatus, instruments, books, charts and chemicals, such as are not published nor made in the United States, when expressly imported in good faith by and for the use of any regularly established or incorporated university, college, academy, school, seminary of learning, or free public library, and not intended for sale; and the Secretary of the Treasury shall make suitable regulations to carry out the intent of this paragraph."

As it is evident that this section fails to afford relief to educational institutions ; that it will restrict research ; and practically levies a tax on knowledge, your committee, on motion of Dr. C. F. Chandler, recommend that Sec. 629 be amended to read as follows :

" Scientific apparatus, instruments, utensils, and implements, chemicals and chemical preparations, including the bottles and boxes containing the same ; books, periodicals of all kinds, maps, charts, etchings, engravings, and lithographic prints ; when expressly imported in good faith by and for the use of any regularly established or incorporated university, college, academy, school, seminary of learning, or free public library ; and not intended for sale ; and the Secretary of the Treasury shall make suitable regulations to carry out the intent of this paragraph."

Your committee recommend that this proposed amendment be referred to the Council of the American Chemical Society for their approval and transmission to the United States Senate in the name of the Society.

Further, as it is believed "that by concerted action something may be accomplished, but if each person makes a separate and distinct proposition nothing can be done," it is recommended that this report be at once printed in the Journal of the American Chemical Society, and that the proper authorities at our institutions of learning be requested to indorse this proposition by petitioning the Senate in its behalf.

Very respectfully,

CHARLES E. MUNROE, Chairman.

A new contract between the Society and the Chemical Publishing Co. was approved April 29, 1897.

Certain amendments to the proposed new constitution were referred to the Committee on New Constitution, May 10, 1897.

The bills for printing the February number of the Journal, amounting to \$347.04, and those for printing the March number, amounting to \$353.60, were approved April 30, 1897.

#### NEW MEMBERS ELECTED MAY 4, 1897.

Bauer, William C., Univ. of Cincinnati, Cincinnati, O.  
 Hillyer, William E., 412 A St., S. E., Washington, D. C.  
 Krause, Albert H., 41 Mueller, Ave., Cleveland, O.  
 McFarlen, Thomas J., New Glasgow, Nova Scotia.  
 Prochazka, John, 15 E. 12th St., N. Y. City.  
 Ritchey, James Warren, 701 Baymiller St., Cincinnati, O.  
 Sohon, M. D., Chemical Laboratory, Navy Yard, N. Y.  
 Toch, Maximilian, 468-472 West Broadway, N. Y. City.  
 Tone, Frank Jerome, University Club, Niagara Falls, N. Y.

#### CHANGES OF ADDRESS.

Boot, J. C., care of American Sugar Refining Co., Jersey City, N. Y.  
 Carney, J. A., care of C. B. & Q. Ry. Co., Beardstown, Ill.  
 Davis, W. Walley, care of Norfolk & Western Railroad, Roanoke, Va.  
 Getman, F. A., 196 Atlantic St., Stamford, Conn.  
 Mathews, John A., 4 First Place, Brooklyn, N. Y.  
 Meade, R. K., Lafayette College, Easton, Pa.  
 Parker, Chas. E., 150 Alden St., Orange, N. J.  
 Power, Fred. B., care of Burroughs, Wellcome & Co., Snow Hill Buildings, London, E. C., England.  
 Tuckerman, Alfred, Townsend Building, Cor. 25th St. and Broadway, N. Y. City.  
 Wallace, E. C., foot of 6th St., Long Island City, N. Y.

Wickhorst, Max. H., Eng. of Tests, C. B. & Q. Ry., Aurora,  
Ill.

Wood, Jos. R., 820 President St., Brooklyn, N. Y.

**ADDRESS WANTED,**

Peters, Andrew, formerly of 301 Schiller St., Chicago, Ill.

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**MEETINGS OF THE SECTIONS.**

**WASHINGTON SECTION.**

The ninety-fifth regular meeting of the Chemical Society of Washington was called to order at 8 P.M. in the Cosmos Club Hall by the president, Dr. Bigelow, with thirty-one members present.

The first paper "Three Early American Chemical Societies" was read by Dr. H. Carrington Bolton, who presents the following abstract:

"The first chemical society ever organized in either hemisphere was founded at Philadelphia in 1772, forty-nine years before the Chemical Society of London, the oldest in Europe. The president was Dr. James Woodhouse, Professor of Chemistry in the Medical Department of the University of Pennsylvania, and the first vice-president was Felix Pascalis Ouvrière, a naturalist born in France and for some time a resident of Santo Domingo. On December 10th, 1801, Robert Hare presented to the Chemical Society of Philadelphia his memorable paper on the "Hydrostatic Blowpipe," which was published by the Society in the following year as a pamphlet with the title: "Memoir on the Supply and Application of the Blowpipe."

In 1811 a second chemical society was founded in Philadelphia called the "Columbian," under the presidency of Prof. James Cutbush. The constitution of this Society provided for levying fines on absent members and those who refused to accept office when elected. The Society numbered sixty-nine members, of which thirty-one were foreign chemists, and thirteen junior members; these included the most prominent chemists and philosophers living on both sides of the Atlantic. In 1813 the Columbian Chemical Society of Philadelphia published one

volume of memoirs; this contained twenty-six essays on a variety of topics original, speculative, and practical.

The third chemical society was the Delaware Chemical and Geological Society, organized at Delhi, New York, in 1821. It was, however, short-lived and issued no publications.

Dr. Bolton's essay contained brief biographical sketches of the prominent members of these societies.

The second paper, on "The Experimental Determination of the Hydrothermal Value of a Bomb Calorimeter," was read by H. W. Wiley and W. D. Bigelow. "The methods previously suggested by other authors for this purpose were reviewed, and their advantages and disadvantages discussed. The authors employed a relatively large body of warm water instead of a very small portion, as has previously been used. The amount of water used in the bomb under discussion which was exhibited and described at the meeting, was about 1800 cc. In the determination of the hydrothermal value approximately 1000 cc. was first added and the rate of change of temperature observed. About 800 cc. of water at a temperature approximately 10° higher than the first employed was then added, after observing its temperature and rate of change of temperature. Two Beckmann thermometers were used, by which it is possible to read the temperature to thousandths of a degree, so that the error which would otherwise arise from the slight change of temperature was overcome by the accuracy in the reading of the thermometer."

The last paper "On the Influence of Vegetable Mold on the Nitrogenous Content of Oats" was read by Dr. Wiley. Attention having been called several years ago to the large increase in the nitrogen in sugar cane grown in the muck soils of Florida, an investigation was instituted by the Department of Agriculture in 1894 to determine in what way the humus of such soils influenced the nitrogen contents of cereal crops. The first year's investigation was preliminary, but it showed distinctly that oats grown on soils rich in vegetable mold contained a larger percentage of nitrogen than that grown in other soils. The total increase is in general about twenty-five per cent. This increase was not in the grain alone but also in the straw. The second year's investigation verified this result. The increase was largely in amid nitrogen, the percentage of pro-

teids not being greatly increased. The results are therefore not so interesting from an economic point of view. When it is remembered that these vegetable soils are extremely rich in nitrogen and when it is further considered that they are quite deficient in nitrifying organisms, it is fair to conclude that at least a portion of this excess of nitrogen which they contain is assimilated directly from the vegetable mold without previous oxidation to nitric acid. Data was adduced which showed that the addition of phosphatic fertilizers tended to diminish the actual percentage of nitrogen in the crop harvested.

At the end of the regular program, Prof. R. B. Warder exhibited some photographs which showed the power of various chemical substances to absorb X-rays, and explained the technique of the manipulation.

V. K. CHESNUT.

#### NEW YORK SECTION.

The April meeting of the section was held at the College of the City of New York, at 8.15 P.M., April 9th, Prof. McMurtrie presiding.

The minutes of the March meeting were omitted.

The following papers were read: "Historical Note on the Estimation of Fat in Desiccated Products," by W. E. Chamberlain; "Mechanical Construction for Chemists," by Walter D. Field; "On the Manufacture of Dynamite," by G. E. Barton; "On the Estimation of Carbon Dioxide associated with Sulphur Dioxide in the Binary Liquid," by C. F. McKenna; "Interpretation of Starch Determinations," by H. C. Sherman; "Organic Compounds Used in Medicine," First paper, Aliphatic Compounds, by Marsten T. Bogart.

A special meeting of the New York Section of the American Chemical Society was held in the Chemical Lecture Room of the College of the City of New York, on Friday evening, April 23, at 8.15 o'clock.

This meeting was appointed for the discussion of "The Value of Bacteriological Examination of Water from a Sanitary Point of View," and was opened by a paper on the subject by Dr. Edward K. Dunham, Director of the Carnegie Laboratory, in New York City.

Dr. C. B. Dudley, President of the Society, presided, and the

following specialists took part in the discussion: Dr. W. T. Sedgwick, Director of the Biological Laboratory of the Massachusetts Institute of Technology, Boston; Dr. J. J. Kinyoun, U. S. Marine Hospital Service, Washington, D. C.; Dr. W. P. Mason, Rensselaer Polytechnic Institute, Troy, N. Y.; Dr. A. R. Leeds, Stevens Institute, Hoboken, N. J.

Eighty-five members were present.

The regular monthly meeting of the New York Section of the American Chemical Society was held at the College of the City of New York on Friday evening, May 7, Dr. W. McMurtrie presiding. The ferrocyanides of zinc and manganese were very fully discussed in papers by Mr. George C. Stone and D. A. Van Ingen, and E. H. Miller and J. A. Mathews. Prof. Auguste J. Rossi read a paper on "Titanium and Some of Its Compounds," exhibiting specimens of compounds of titanium with silicon, boron, etc., and cited analyses to show that titanium will enter into compounds in the same manner as silica.

Samples were shown containing 65 per cent. titanic acid, 14.30 per cent. lime, 10.50 per cent. alumina, 9.34 per cent. magnesia, 0.90 per cent. iron, 0.67 per cent. silica, with many others containing large amounts of titanic acid.

Dr. Doremus exhibited a number of specimens prepared by Prof. Henri Moissan with his electric furnace for the Smithsonian Institution, which had just arrived, including tungsten, titanium, vanadium, uranium, chromium, molybdenum, a carbide of tungsten bearing the same relation to metallic tungsten as cast iron to wrought iron; borides of iron and carbon, and, not the least interesting, fused lime.

Prof. M. T. Bogert read his second paper on "Organic Compounds Used in Medicine," describing very fully the properties of the aromatic compounds, including phenol, aseptol, eugenol, guiacol, resorcinol, benzo-naphthol, saccharine, etc., as to both chemical and physiological peculiarities. Among the seventy members present were Drs. E. R. Squibb, E. H. Bartley, William H. Chandler, A. C. Hale and C. A. Doremus. The meeting was adjourned at 10.30 P. M. to June 11, which will be the last of the season.

## CINCINNATI SECTION.

The May meeting of the Section was held on May 15th in the Chemical Lecture Room of Hanna Hall, University Buildings, Prof. J. U. Lloyd in the Chair.

A communication was read from Mr. E. C. Wallace, in which he tendered his resignation as president and as a member of the Section, owing to his removal to New York City. The resignation was accepted and a resolution adopted, expressing the regret and good wishes of the Section, to be forwarded to Mr. Wallace. Dr. Wm. L. Dudley was elected President of the Section.

Dr. J. N. Hurty then read a paper "On the Determination of Crude Fiber in Cereals."

The author was under the necessity of devising a method more rapid than the official method, owing to the great number of samples of whole wheat flour to be operated upon, and arrived at the following mode of procedure :

Two grams of the air-dried flour were weighed into a 500 cc. beaker, 200 cc. of saturated solution of salt added, which was immediately acidulated with five cc. of hydrochloric acid of specific gravity 1.16. This was quickly brought to a boil on a hot plate, the boiling being continued for ten minutes. The starch was completely hydrolyzed within this time, and the albuminoid content in part dissolved, but a large portion is transformed into a condition so fine as to remain suspended in the liquid, making it opalescent. The insoluble matter is caught on a Gooch filter, washed thoroughly with hot water, then with 200 cc. of hot two per cent. solution of sodium hydroxide, then with water again, followed by alcohol and petroleum ether. The Gooch filter and its contents are then dried at 110° C., weighed and ash subtracted.

Twenty minutes suffice to do all this except the drying and burning. The average of five fiber assays of a certain whole wheat flour by the official method, was 2.48 per cent.; by the "salt method" the average found on the same material was 2.53 per cent. A sample of bran gave as an average of five assays by the official method 11.84 per cent., by the "salt method" 11.91 per cent.

The author then gave the results of some additional experi-

ments on the same material, using diastase to convert the starch into sugar, and pepsin to render the albuminoid matter soluble. By this method the average of three crude fiber assays of the same whole wheat flour used in the former experiments was 10.33 per cent, this residue containing nitrogen and substances convertible into sugars reducing Fehling's solution. The author intends to continue this line of experiments.

Mr. B. M. Gilhashy then read a paper on "Ozone, its Commercial Production and Application," among other points describing the principal apparent merits of Mr. E. Andreoli's "Open Ozonizer," recently brought before the London Section of the Society of Chemical Industry.

Dr. Hurty finally demonstrated the use of a formaldehyde generator evolved in his laboratory, and an interested discussion on the subject of formaldehyde and ozone concluded the meeting.

S. WALDBOTT.

Issued with July Number, 1897.

## Proceedings.

### BOARD OF DIRECTORS.

The Board of Directors has authorized the establishment of a local section of the American Chemical Society in Columbus, Ohio, the necessary steps having been taken as required by the constitution of the Society.

### COUNCIL.

A proposition to print the titles, degrees, etc., after each name in the annual directory was negatived, June 5th, by a large majority.

### CHANGES OF ADDRESS.

Brown, Thomas, Jr., care of Geo. P. Good & Co., 85 N. Pryor St., Atlanta, Ga.

Fosler, Wm., Jr., Hartford, Ohio County, Ky.

Hero, Ann, 1213 Third St., New Orleans, La.

Herreshoff, J. B. L., 19 Pierrepont St., Brooklyn, N. Y.

Joslin, Prof. Carrie E., 930 Curtiss St., Walnut Hills, Cincinnati, O.

Kellez, J. H., 6030 Ellis Ave., Chicago, Ill.

Lenher, C. A., 871 W. 22d St., Chicago, Ill.

Myers, H. Ely, 5170 Butler St., Pittsburg, Pa.

Vinson, Elbert E., Ohio State Univ., Columbus, O.

Wickhorst, Max H., Engineer of Tests, C. B. & Q. R. R., Aurora, Ill.

### ADDRESSES WANTED.

Peacock, Samuel, formerly of Station 1, Philadelphia, Pa.

Peter, Alfred M., formerly of 236 E. Maxwell St., Lexington, Ky.

### MEETINGS OF THE SECTIONS.

#### NEBRASKA SECTION.

A meeting of the Nebraska Section was held Thursday evening, June 3d, in the chemical laboratory of the State University.

The Section was called to order at 7.30, President Nicholson in the chair.

The minutes of the previous meeting having been read and approved, the Secretary's and Treasurer's reports for the past year were read and adopted.

Officers for the coming year were then elected, the result of the election being as follows :

President—H. H. Nicholson.

Secretary and Treasurer—John White.

Executive Committee—Samuel Avery, R. S. Hittner and Rosa Bouton.

The President's address was then delivered. It consisted of a brief resumé of the development of chemistry in Nebraska, especially in the University, and pointed out in what way the existence of the Section had been, and could be, beneficial to this development. Dr. Avery read a paper embodying recent researches on "Some Phenylidicarboxallilic Acids and Their Derivatives."

The audience then adjourned to the lower rooms of the laboratory, where a very dainty repast was served by the ladies of the Section ; various pieces of chemical apparatus being made to do duty for quite unheard-of purposes. A number of toasts were responded to in a bright, entertaining manner, and the Section voted that the second year of its existence had been very pleasantly brought to a close.

JOHN WHITE.

#### RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence on Thursday evening, May 20, 1897, Chairman E. D. Pearce presiding.

Mr. F. P. Gorham read a paper upon "Bacteria and their Products." The reader gave the history of the discovery of bacteria, mentioning spontaneous generation and cause of disease, as understood in the early times. The products of activity of bacteria, including pigment, gas and acid production, fermenting liquifying gelatine, and the formation of toxins were discussed. The application of bacterial cultures to butter-making in agriculture and cure of disease was mentioned. At the close of the paper Mr. Gorham exhibited, under the microscope, preparations of diphtheria, tuberculosis, typhoid and anthrax bacillus.

## NEW YORK SECTION.

The New York Section of the American Chemical Society held its June meeting on the 11th, preceded by a dinner, at which thirty members participated, among whom were Dr. Charles B. Dudley, president of the Society.

The meeting was called to order in the chemical lecture room of the College of the City of New York, at 8.30, by the Chairman, Dr. William McMurtrie, who then invited Dr. Dudley to preside.

The death of Prof. C. R. Fresenius, at Wiesbaden, was announced, and the secretary was authorized to cable the regrets and condolence of the Society to his sons. An obituary notice of Dr. Carl H. Schultz was read by Dr. A. P. Hallock, after which the papers of the evening were read as follows:

"Comparative Tests for Identification of Some Medicinal Carbon Compounds," by F. S. Hyde; "Note on the Analysis of Cheese," by E. G. Love; "Determination of Dextrine in Presence of Sugars," by Benj. C. Greenbergh; "Novel Mechanical Arrangement of Fat Extraction Apparatus," by Gustav Volckening; "Demonstration of Some Chloroform Compounds and of Some of Bauman's Thioaldehydes," by L. Reuter; "Calibration of Volumetric Apparatus," by W. E. Chamberlin; "Method of Collecting and Analyzing Gases Contained in Canned Goods," by C. A. Doremus.

It was stated by the chair that forty papers had been presented before the Section during the winter, a number considerably in excess of any previous session, and the attendance at the meetings had averaged about fifty, also an increase over previous records.

The Section was then adjourned until October.

DURAND WOODMAN.

## WASHINGTON SECTION.

The ninety-sixth regular meeting of the Chemical Society of Washington was held in Cosmos Club Hall, Washington, D. C., May 13, 1897. The Society was called to order at 8 p. m. by the President, Dr. Bigelow, with twenty-seven members present, and the following program presented:

"The Chloronitrides of Phosphorus," by H. N. Stokes;

"The Ripening of Cheese and the Rôle which Micro-organisms Play in the Process," by P. Fireman; "The Products of the Tuberculosis Bacillus," by E. A. de Schweinitz and Marion Dorset; "The Standard Methods of Starch Determination," by H. W. Wiley and W. H. Krug; "The Commercial Preparation of Nitronaphthalene," by W. H. Krug and J. E. Blomén; "The Replacement of Chlorine by Sulphur in Alkaline Chlorides," by F. K. Cameron; "A New Mineral," by Wirt Tassin.

Dr. Stokes showed that "The only members of the phosphorus chloronitride series,  $(\text{PNCl}_n)_n$ , hitherto known are  $(\text{PNCl}_1)_n$ , (Liebig), and  $(\text{PNCl}_2)_n$ , (Stokes). The series is now extended to include  $(\text{PNCl}_3)_n$ ,  $(\text{PNCl}_4)_n$ , and  $(\text{PNCl}_5)_n$ , as well as a mixture of higher polymers, not yet isolated, and terminating with a rubber-like polymer of high molecular weight. The substances are prepared by heating equimolecular weights of phosphorus pentachloride and ammonium chloride in sealed tubes, whereby a mixture of chlorides in nearly theoretical amount is obtained. This is distilled from the open tube and afterwards submitted to careful fractional distillation *in vacuo*. The unique feature of the series is found in the fact that any member can be converted into the rubber-like polymer by heating, and that the latter on distilling at a higher temperature breaks down quantitatively into a mixture of all the lower members; it is therefore possible ultimately to convert any member completely into any other by heating and distilling alone. The lower members, up to and including  $(\text{PNCl}_1)_n$ , are well characterized, finely crystallized bodies, while  $(\text{PNCl}_2)_n$  is liquid. Their stability diminishes with increasing molecular weight,  $(\text{PNCl}_5)_n$  being unattacked by boiling alkalies, while the rubber-like polymer is destroyed by boiling water. The formation of  $\text{PNCl}_1$  and  $(\text{PNCl}_2)_n$  could not be detected. The chloronitrides constitute the first extended series of inorganic polymers interconvertible by simple and direct means."

Dr. Fireman gave an extended resumé of the work of Duclaux and others, showing that the lactic acid producing bacteria are not so important in the production of butter flavors, as are the peptonizing bacteria.

Drs. de Schweinitz and Dorset present the following abstract of their paper: "In studying the products of the growth of the

tuberculosis bacilli in artificial media, it was noted that the reaction of the cultures usually becomes acid, and as Prudden and Hodenpyl had succeeded in producing tuberculous nodules without necrosis, by the intravenous injection of dead bacilli, it seemed as though it should be possible to isolate from cultures of tuberculosis bacilli, an acid substance, which is responsible for the necrosis of tissue that always takes place in this disease. After many fruitless attempts, we succeeded in isolating from artificial cultures a crystalline acid substance having a melting-point of 161° to 164° C., which was soluble in ether, alcohol and water, and crystallized in needle-like prisms. The solution of this substance was optically inactive, and did not give the biuret reaction. The preliminary analysis of this substance gave a formula like that of teraconic acid, and the other properties correspond closely with this acid—its identity, if such, has not as yet been proved. When injected subcutaneously into guinea pigs, it causes a slight inflammation and localized necrosis; and injected directly into the liver tissue by means of a hypodermic syringe, it produces characteristic necrosis. The substance causes a reduction of temperature in tuberculous animals, and it seems probable that we have here the material which is responsible for the necrosis in tubercular infection."

Dr. Wiley and Mr. Krug showed that various methods depending on the polarization of the starch or its inversion products, as well as others based on direct mingling of the starch, were too inaccurate to commend themselves to the analyst. The only accurate methods depend on the eventual inversion of the starch into dextrose, which is then estimated by Allihn's method.

Experiments in the preparation of the nitronaphthalene showed that they cannot be prepared from  $\alpha$ -naphthalene sulphonic acid, but that the best yield is obtained with mixtures of nitric and sulphuric acids. The best results were obtained with 30° B. nitric acid, using about three times as much acid as naphthalene. The amount of sulphuric acid used varies with the nitration degré desired, varying from 4 : 1 (nitric : sulphuric) for low melting products, to 3 : 2 for the higher derivatives.

Dr. Cameron cited some of his own experiments to show that,

although it is possible in the case of some heavy metals, to replace chlorine by sulphur by merely boiling the latter with a solution of the chloride, it is impossible to obtain such a reaction with the alkaline or alkaline earth chlorides, even upon heating in sealed tubes at a high temperature.

Mr. Tassin gave a short description of a new mineral, but reserves the details for special publication.

V. K. CHESNUT.

Issued with August Number, 1897.

## Proceedings.

### NEW MEMBERS ELECTED JULY 16, 1897.

Burn, H., Sloss Iron and Steel Co., Birmingham, Ala.  
Clafin, Alan A., Littleton, Mass.  
Commiskey, Archibald F., 155 Sixth Ave., Brooklyn, N. Y.  
Driessen, Peter A., 188 State St., Brooklyn, N. Y.  
Fahlberg, Dr. Constantin, Salbke bei Magdeburg, Germany.  
LaBach, James O., 4222 North Cherry St., Cincinnati, O.  
Luster, Herbert A., 28 Prospect St., Elizabeth, N. J.  
Martin, Henry G., Coatesville, Pa., care of Lukens Iron and  
Steel Co.  
Palmer, Chas. Skeele, Box 643, Boulder, Colo.  
Poole, Herman, 323 W. 34th St., N. Y. City.  
Test, Wm. Henry, Purdue Univ., Lafayette, Ind.  
Tone, Hugo, Consumers Ice Co., 36th and Butler Sts., Chi-  
cago, Ills.

### ASSOCIATES ELECTED JULY 16, 1897.

Hashvanter, Chas., 159 Front St., N. Y. City.  
Hill, Hibbert, Rockville Centre Lab., Rockville Centre, Long  
Island.

### NEW MEMBERS ELECTED JUNE 19, 1897.

Colby, Edward A., 411 N. J. R. R. Ave., Newark, N. J.  
Evans, Ernest, Mingo Junction, Jefferson Co., O.  
Gustin, G. H., Elizabeth, N. J.  
Marschall, Adolf J., Little Falls, N. Y.  
McKenzie, R. Monroe, Chem. Dept. Univ. of Cin., Cincinnati, O.  
Newell, Lyman C., English High School, Somerville, Mass.  
Nishkian, P. F., care Armour Packing Co., Kansas City, Mo.  
Reinus, Barnhard, Paterson Chem. Works, First Ave., Pat-  
erson, N. J.  
Reuter, Ludwig H., Merck Building, N. Y. City.  
Sedding, Geo. H. P., Anita, Citrus Co., Fla.  
VanGelder, Arthur Pine, Columbia Univ., N. Y. City.

### ASSOCIATES ELECTED JUNE 19, 1897.

Buck, John, 235 Kent Ave., Brooklyn, N. Y.  
Cochran, Alfred, 931 Lafayette Ave., Brooklyn, N. Y.  
Lindsay, Gordon L., 348 W. Fourth St., Cincinnati, O.  
Oshorn, George Augustus, Box 807, Asbury Park, N. J.  
Parrott, Ralph Brewster, Schoharie, N. Y.  
Winters, H. Lloyd, 635 Madison St., Brooklyn, N. Y.

## CHANGES OF ADDRESS.

Alexander, Jerome, 502-510 W. 45th St., N. Y. City.  
 Becher, Jesse B., High School, Sioux City, Iowa.  
 Beeson, J. L., Ga. Nor. & Indus. College, Milledgeville, Ga.  
 Bevier, Miss Isabel, Plymouth, Ohio.  
 Brinker, Harry L., 619 Crosman Ave., Youngstown, Ohio.  
 Bromwell, Wm., 264 Ryerson St., Brooklyn, N. Y.  
 Bryan, A. Hugh, 1414 N. Illinois St., Indianapolis, Ind.  
 Buck, John, 235 Kent Ave., Brooklyn, N. Y.  
 Burk, W. E., Box, Plumas Co., Cal.  
 Burwell, A. W., 33 Atwater Bldg., Cleveland, O.  
 Chazal, P. E., Box 284, Charleston, S. C.  
 Cochran, C. B., 514 S. High St., West Chester, Pa.  
 Couch, Guy E., 1303 Central Ave., Cincinnati, Ohio.  
 Cutts, Henry E., 1721 Davenport St., Omaha, Nebr.  
 Dohme, A. R. L., care of Sharp & Dohme, Baltimore, Md.  
 Dorr, John V. N., Box 872, Deadwood, S. D.  
 Dunham, E. K., Seal Harbor, Maine.  
 Griffin, Jas. H., Patent Office, Washington, D. C.  
 Higbee, H. H., Hamilton College, Clinton, N. Y.  
 Hobbs, P. L., Western Reserve Univ., Cleveland, Ohio.  
 Hurlburt, E. B., Glastonbury, Conn.  
 Hurty, J. N., 202 N. Penn St., Indianapolis, Ind.  
 Johnson, S. W., 54 Trumbull St., New Haven, Conn.  
 Kendall, E. Dwight, 417 Clermont Ave., Brooklyn, N. Y.  
 Kirchmaier, G. A., Adams and Huron Sts., Toledo, Ohio.  
 Labonde, Leon, 75 Washington Ave., Newark, N. J.  
 Linebarger, C. E., 359 Dayton St., Chicago, Ill.  
 Lippincott, W. B., care Arkansas Val. Smelter, Leadville, Col.  
 Macy, Sherman R., 3722 Third St., Des Moines, Iowa.  
 Martin, Henry G., care of Lukens Iron and Steel Co., Coatesville, Pa.  
 Miles, G. W., Jr., 103 Milk St., Boston, Mass.  
 Meisel, C. F. A., 402 Washington St., N. Y. City.  
 Palmer, Prof. A. W., Univ. of Ill., Campaign, Ill.  
 Peacock, S., 1019 Market St., Philadelphia, Pa.  
 Pinkerton, David J., Dalzell Steel and Iron Works, Mortherwell, Scotland.  
 Richards, J. W., 1802 Catharine St., Philadelphia, Pa.  
 Rosell, C. A. O., Litho Bldg., N. Y. City.  
 Schroeder, J. Henry, Jewish Hospital, Cincinnati, Ohio.  
 Sherman, H. C., Maryland Agricul. College, College Park, Md.  
 Tennille, Geo. F., 77 Carnegie Ave, East Orange, N. J.  
 Thompson, Firman, New Carlisle, Ohio.  
 Trescot, Thomas C., Century Club, Washington, D. C.  
 Wakeman, Alfred J., 359 W. Boulevard, N. Y. City.  
 Williams, Wm. J., 2215 Bridge St., Frankford, Philadelphia, Pa.

Issued with September Number, 1897.

## Proceedings.

### COUNCIL.

#### CHANGES OF ADDRESS.

Andrews, Geo. F., Sec'y Amer. Seamless Wire Co., Providence, R. I.

Auchy, 3606 Washington St., Tacony, Philadelphia, Pa.

Austen, Peter T., Amer. Pegamoid Co., 11 Broadway, N. Y. City.

Baumgarten, F. M., 390 LaFayette Place, Milwaukee, Wis.  
Dunlap, Chas. J., Watertown, N. J.

Fourneaux, E. A., Box 284, Pawtucket, R. I.

Graham, W. H., Sunnyhurst, Trowbridge, Wilts, England.

Hancock, David, care Birmingham Rolling Mill Co., Birmingham, Ala.

Harms, Armin, care Compania Metallurgica Mexicana, San Luis Potosi. Mex.

Hurlburt, E. B., care The J. B. Williams Co., Glastonbury, Conn.

Kilgore, B. W., Agricultural College, Miss.

Macdowell, W. F., Med. Dept. U. S. Imm. Service, Barge Office, N. Y. City.

Meeker, G. H., Medico-Chirurgical College, 18th and Cherry Sts., Philadelphia, Pa.

Perry, Chas. M., 324 Rochambeau Ave., Providence, R. I.

Peter, Alfred M., 236 E. Maxwell St., Lexington, Ky.

Takamine, Jokichi, 511 Chamber of Commerce Bldg., Chicago, Ill.

Vocum, John H., 30 Ferry St., N. Y. City.

#### ADDRESS WANTED.

Anderson, Chas. A., formerly of Flat 2, 2409 Wabash Ave., Chicago, Ill.

#### MEETINGS OF THE SECTIONS.

##### NORTH CAROLINA SECTION.

The Summer meeting of the North Carolina Section of the American Chemical Society was held in the Chemical Department of Wake Forest College, June 25, 1897, with Dr. F. P.

Venable, chairman of the section, in the chair, and twelve members present.

The following papers were read and discussed:

1. "Notes on Some Halogen Compounds of Zirconium." By F. P. Venable and Chas. Baskerville.
2. "Note on the Relation of Humus to Soil Fertility." By W. A. Withers and J. S. Buffalo.
3. "Reaction between Concentrated Sulphuric Acid and Mercury." By Chas. Baskerville and F. W. Miller.
4. "Some Further Work on the Volumetric Estimation of Phosphoric Acid." By B. W. Kilgore.
5. "Development of our Knowledge of the Iodonium Bases." By W. A. Jones.
6. "Spelling of Chemical Terms." By F. P. Venable.

The resignation of B. W. Kilgore as secretary was accepted, and W. A. Withers elected to fill the vacancy.

The section is growing in interest and usefulness.

B. W. KILGORE.

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#### RHODE ISLAND SECTION.

The annual meeting of the Rhode Island Section of the American Chemical Society was held in the Hope Club, Providence, June 10, 1897, with Chairman Edward D. Pearce presiding. The following officers were elected for the ensuing year: Edward D. Pearce, Chairman; Walter E. Smith, Secretary and Treasurer; Charles S. Bush a member of the executive committee.

After dinner the Chairman, Mr. Edward D. Pearce, presented a paper on the "Sources and Distribution of Sulphur." The reader discussed the comparative merits of the different varieties of sulphur ores and showed samples of ore from the principal sources.

WALTER E. SMITH.

Issued with October Number, 1897.

## Proceedings.

### FIFTEENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The Fifteenth General Meeting of the American Chemical Society was held in connection with the meeting of Section C of the American Association for the Advancement of Science, in Detroit, Mich., August 9 and 10, 1897.

According to a previous arrangement between the two bodies, Section C met for organization on Monday morning of the Association week and also late on Monday afternoon to listen to the address of the Vice-President of that section. The balance of Monday and the whole of Tuesday were devoted to the sessions of the American Chemical Society and the remainder of the week to those of Section C.

The papers offered to the two bodies were put together and classified according to the subjects of which they treated, each session of the week being devoted to one or more of the subjects considered, the final disposition of the papers for publication being determined by their respective authors.

#### MONDAY MORNING.

The first session of the American Chemical Society was held jointly with that of Section C on Monday morning, immediately after the election of officers of Section C, in room 130 of the Central High School building, where all subsequent sessions of the society were also held. President Chas. B. Dudley and Vice-President Wm. P. Mason, of Section C, were both upon the platform. By the courtesy of Dr. Mason, President Dudley was called upon to preside.

Hon. Wm. C. Maybury, Mayor of Detroit, was introduced and gave a very cordial welcome to the visiting chemists. President Dudley responded in behalf of the American Chemical Society, and Vice-President Mason in behalf of Section C.

The morning session was then adjourned.

#### MONDAY AFTERNOON.

The afternoon session was called to order at 2.20 P.M. Papers were read and discussed in the following order :

"The Action of Oxide of Manganese on Potassium Permanganate." By Charles L. Reese. Discussed by Messrs. Conradson and Reese.

"Contributions to the Chemistry of Didymium." By L. M. Dennis and E. M. Chamot. Read by Mr. Dennis. Discussed by Messrs. Dudley, Mason, and Dennis.

"Some New Compounds of Hydronitric Acid." By L. M. Dennis and C. H. Benedict. Read by Mr. Dennis.

"On Two Polymeric Series of Phosphorus-Nitrogen Compounds, and on the Stereochemistry of Phosphorus and Nitrogen." By H. N. Stokes. Read by E. F. Smith in the absence of the author.

The following named papers were read by title :

"The Action of Nitric Acid upon Aluminum and the Formation of Aluminum Nitrate." By T. B. Stillman.

"On the Action of Nitric Acid on Metals." By G. O. Higley.

The General Secretary presented an informal report, showing the present membership of the society to be : Members, 1018 ; associates, 78 ; honorary members, 7. Total, 1103.

Since the annual meeting, last December, the society has lost by death the following named members : Prof. T. G. Wormley, Philadelphia ; T. A. Havemeyer, New York ; Dr. Carl H. Schultz, New York ; and Prof. Edgar McClure, Eugene, Oregon.

Dr. E. R. Squibb and Prof. John H. Appleton have resigned from the Council, and their places have been filled by Prof. W. A. Noyes, of Terre Haute, and Dr. A. A. Noyes, of Boston.

Reports of special committees upon the following subjects were then presented :

On Spelling and Nomenclature for the Journal, Edward Hart, Chairman; on Coal Analysis, W. A. Noyes, Chairman; on Standard Color for Water Analysis, A. R. Leeds, Chairman. (Oral report by W. P. Mason, in the absence of the chairman.)

The editor made an oral report regarding the Journal and its publication, and President C. B. Dudley made some remarks concerning the reports and work of the Committees on Coal Analysis and Duty-free Importations. Dr. Hart followed with the statement that through the efforts of the Committee on Duty-free Importations certain very important changes had been made in the text of the Dingley bill in Congress.

After some announcements the session was adjourned to give the chemists the opportunity of listening to the address of Vice-President Wm. P. Mason, before Section C of the American Association for the Advancement of Science.

#### TUESDAY MORNING.

At eight o'clock about thirty of the members visited the chemical works of F. Stearns & Co., upon invitation of the company.

At the hour for the session the society was called to order and President Dudley introduced Prof. A. Vernon Harcourt, of Oxford, England, who followed with some very interesting remarks appreciative of American chemists and their work.

Papers were then read in the following order :

"Alkyl Bismuth Iodides." By A. B. Prescott.

"Kola Tannin." By A. B. Prescott.

"The Chemistry of Methylene." By J. U. Nef. Discussed by A. Vernon Harcourt and Messrs. Dudley, Barker, Nef, and E. F. Smith.

"On the Constitution of Some Hydrazones." By Paul C. Freer.

The morning session was then adjourned.

#### TUESDAY AFTERNOON.

The report of the Committee on Triennial Congress of Chemists, F. W. Clarke, Chairman, was read by the Secretary. At the request of the chairman, received by letter, the committee was discharged, the society extending its thanks for the work done.

The thanks of the society, for courtesies received, were unanimously voted to the Local Committee of the American Association for the Advancement of Science, and especially its Secretary, Mr. John H. Russell; the Mayor and citizens of Detroit; the officers and members of Section C of the American Association for the Advancement of Science for their cooperation in the meeting; the local press; and the officials of the various works visited by the chemists.

After some announcements, papers were read as follows:

"On the Determination of the Volatility of Phosphorus Pentoxide." By E. W. Morley.

"On the Action of Sodium on Methylpropylketon and on Acetophenon." By Paul C. Freer.

"Recent Progress in Analytical Chemistry." By L. M. Dennis.

The following named papers were read by title:

"Derivatives of Eugenol." By F. J. Pond and F. T. Beers.

"Qualitative Analysis; a Point in Teaching that Was Not a Full Success." By A. L. Green.

"A New Color Standard for Use in Water Analysis." By Ellen H. Richards.

The Fifteenth General Meeting of the American Chemical Society was then adjourned.

*Notes.*—1. The report of the Committee on Duty-free Importations has been received since the adjournment of the meeting.

2. At the close of the session on Tuesday afternoon the chemists visited the chemical works and biological laboratories of Parke, Davis & Co., where they were received with the greatest hospitality; all departments of the works, etc., were shown to them; and after their inspection of these a lunch was furnished by Messrs. Parke, Davis & Co., and a special exhibition of the efficiency of the fire department of the establishment was witnessed.

ALBERT C. HALE, General Secretary.

**COUNCIL.**

The new constitution, as amended, was adopted September 28th. This will be printed and separately distributed to members.

The next meeting of the society will be held in Washington, December 29th and 30th.

**NEW MEMBERS ELECTED SEPTEMBER 10, 1897.**

Attix, James C., care Andover Iron Co., Phillipsburg, N. J.  
 Blackmore, Henry S., 206 S. 9th Ave., Mt. Vernon, N. Y.  
 Browning, Dr. Philip E., Yale College, New Haven, Conn.  
 Doan, Miss Martha, Industrial Training School, Indianapolis, Ind.  
 Duffield, Dr. Samuel P., 274 Kirby Ave., W. Detroit, Mich.  
 Edgar, Clinton G., care Detroit Gas Co., Detroit, Mich.  
 Fielding, Frank E., Virginia City, Nev.  
 Flintermann, Prof. R. F., State School of Mines, Rapid City, S. D.  
 Francis, John M., care Parke, Davis & Co., Detroit, Mich.  
 Freer, Prof. Paul C., Ann Arbor, Mich.  
 Haley, E. J., Ridgway, Pa.  
 Jones, Wm. App., Hillsboro, N. C.  
 Kuntz, Louis A., Natrona, Pa.  
 Manns, Albert G., care Armour & Co., U. S. Yards, Chicago.  
 Miller, P. S., Stillwater, Saratoga Co., N. Y.  
 Morley, Prof. Edward W., Cleveland, O.  
 Murrill, Paul I., care Parke, Davis & Co., Detroit, Mich.  
 Pinkerton, David J., Dalzell S. and I. Works, Motherwell, Scot.  
 Shattuck, A. F., Solvay Process Co., Detroit, Mich.  
 Tibbals, Wm. I., Health Office, Detroit, Mich.  
 Whitney, Willis R., Mass. Inst. Tech., Boston, Mass.  
 Willy, Ogden, 7749 Reynolds Ave., Chicago, Ill.

**ASSOCIATES ELECTED SEPTEMBER 10, 1897.**

Foster, Albert D., 124 Charlotte Ave., Detroit, Mich.

**CHANGES OF ADDRESS.**

Berghausen, E. J., 644 Crown St., Cincinnati, Ohio.  
 Bevier, Isabel, Guilford House, Cleveland, Ohio.  
 Blair, A. W., Agr. Expt. Sta., Raleigh, N. C.  
 Dunham, Edward K., 338 E. 26th St., N. Y. City.

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Graves, W. G., 555 Sibley St., Cleveland, Ohio.  
Guild, F. N., Univ. of Ariz., Tucson, Ariz.  
Saunders, W. M., 20 Bowen St., Olneyville, R. I.  
Schimpf, Henry W., 354 W. 35th St., N. Y. City.  
Shepherd, Frank I., University Park, Colo.  
Sherman, H. C., Columbia Univ., N. Y. City.  
Twitchell, E., 9 Cumberland Flats, Avondale, Cincinnati,  
Ohio.  
Williams, Chas. B., Agr. Expt. Sta., Raleigh, N. C.

Issued with November Number, 1897.

## Proceedings.

### MEETING OF THE BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Engineer's Club, 374 Fifth Ave., New York City, on the evening of October 7, 1897. About a quarter before eight o'clock the Directors sat down to a bountiful collation, to which they had been invited by President Dudley. After the dinner, the Board was called to order for business. There were present Messrs. Dudley, Wiley, Munroe, Hale, Austen, McKenna, Hart, Doremus, Chandler, and McMurtrie.

The minutes of the meeting held November 30, 1896, as printed in the Journal of the Society, were approved.

The Board ratified its former action, which had been taken merely by correspondence, in reference to the following matters:

(a) \$100 was allowed for the expenses of the Treasurer's office.

(b) The establishment of a local section in Columbus, Ohio, was authorized.

(c) The proposition of Mr. M. D. Sohon, with reference to preparing an index of the Journal, was accepted.

The General Secretary was allowed \$125 for the expenses of clerical help during the current year in addition to the amount that had been previously appropriated for that purpose.

The following was voted, subject to the approval of the Council of the Society:

Monthly bills presented by the Secretary for clerical help during the year 1898 shall be approved by the Finance Committee and paid by the Treasurer of the Society, provided that the total sum called for by said bills does not exceed five hundred dollars.

The General Secretary was directed to submit the proposed revised constitution to the Society for the vote of its members, whenever the request to do so should receive the signature of fifteen members, as required by the constitution. He was also authorized to have the proposed constitution printed for said purpose and electrotype plates made.

It was duly moved and carried that a committee of five persons be appointed by the President with power to manage the business of advertising in the Journal.

The following resolutions were separately considered and adopted :

*Resolved*, That a committee of three, with Dr. Wiley as Chairman, be appointed, with power to take charge of a want column in the Journal, and that members of the Society seeking positions, and also persons desiring to employ chemists be allowed three one-half inch insertions *free* in said column.

*Resolved*, That a committee of three, of which the President of the Society shall be Chairman, shall be appointed to take into consideration the matter of abstracts and reviews in the Journal, and upon arriving at their conclusion to report the same to the Directors.

Upon motion of Professor Munroe, the cordial thanks of the Directors were voted to the President of the Society for the hospitalities of the evening, which had been so thoroughly enjoyed by all. The motion was put by Vice-President McMurtrie, and carried with great unanimity and enthusiasm.

The meeting of the Board of Directors was then adjourned.

ALBERT C. HALE, Secy.

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### REPORTS OF STANDING COMMITTEES OF THE SOCIETY READ AT THE DETROIT MEETING.

#### COMMITTEE ON DUTY-FREE IMPORTATIONS.

THE COLUMBIA UNIVERSITY,

WASHINGTON, D. C., August 7, 1897.

DR. C. B. DUDLEY, President of the American Chemical Society.

*Sir*: In response to your request, your Committee on Duty-free Importations reports that owing to the form in which H. R. 379 of the Fifty-fifth Congress, 1st Section, passed the House, your committee drew up a substitute for Section 629 of that bill, which was embodied in its report submitted to you April 22, 1897, and subsequently printed in the Journal of the Society.

This proposed substitute was laid before the Senate Committee and it is gratifying to report that Sections 501, 502, 503, 621, and 638 of the Act as finally passed and as it became a law contain all that your committee asked for.

In presenting its report, your committee transmits the following documents for the archives of the Society :

- A. Tariff bill 1394—H. R. 4864.
- B. H. R. 379. In the Senate of the U. S., April 1, 1897, and as reported to the Committee on Finance.
- C. H. R. 379, as passed by the Senate, July 7, 1897.
- D. H. R. 379, as reported from the Conference Committee.
- E. Report of the Conference Committee.
- F. H. R. 379, as it became law.
- G. Report of the National Academy of Sciences for 1884, containing "Report on Customs Duty on Philosophical and Scientific Apparatus."
- H. Correspondence of your committee since 1894.

These papers and letters have been selected for preservation, as they contain data on the interpretation of the law by customs officers in the past which may be of value for citation in the future.

Especial attention is called to the letters of Professor Josiah P. Cooke, of Harvard University, regarding the first steps taken to place philosophical instruments and material for educational institutions on the free list.

Very respectfully,

CHARLES E. MUNROE, *Chairman.*  
 JOHN HOWARD APPLETON,  
 W.M. L. DUDLEY,  
 EDWARD HART,  
 C. F. CHANDLER,  
 ALBERT B. PRESCOTT,  
 EDGAR F. SMITH.

COMMITTEE ON SPELLING AND NOMENCLATURE FOR THE  
 JOURNAL.

During the year the question of the spelling of the word furfural or furfurol was raised. This word has generally been spelled furfurol. Cross and Bevan had used the spelling furfural, and it was contended that this spelling should be adopted, inasmuch as the word is really an abbreviation of the word furfuraldehyde, which is too long for general use. After considerable correspondence and a full exchange of views, between the members of the committee, this view finally prevailed by a small

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majority. No other business came before the committee during the year.

EDWARD HART, Chairman.

COMMITTEE ON AN INTERNATIONAL CHEMICAL CONGRESS.

WASHINGTON, D. C., August 7, 1897.

The Committee on an International Chemical Congress, appointed in 1893, at Chicago, issued a circular, of which I enclose a copy. A few favorable replies were received from minor organizations, but not from any of the great chemical societies. The attempt, therefore, met with no proper response, and failed. I suggest that the committee be discharged, and that the initiative be left to other organizations.

F. W. CLARKE, Chairman.

[Copy of the circular issued by the Committee on an International Congress of Chemists.]

AMERICAN CHEMICAL SOCIETY,  
September 7, 1894.

To.....

.....

DEAR SIR :

An International Congress of Chemists, organized in connection with the World's Columbian Exposition, was held at Chicago in August, 1893. The American Chemical Society met conjointly with the Congress, and, on account of the interest which was manifested, appointed a Committee of Conference to consider the expediency of holding similar congresses at regular recurrent intervals of time. The geologists have established a series of international congresses, which meet triennially; in medicine and pharmacy similar organizations exist; and in each case the success of the meetings has been very great. The undersigned, therefore, representing the American Chemical Society, respectfully request the chemical societies of the world to appoint similar committees of conference, in order to consider whether it is desirable and practicable to organize a series of International Chemical Congresses, in which the chemists of the various nations can regularly meet together for the discussion of questions of common interest. Hoping for a favorable response, we remain, in behalf of the American Chemical Society,

Very respectfully,

F. W. CLARKE,

CHARLES E. MUNROE,

(Signed) H. CARRINGTON BOLTON,

EDWARD HART,

W. O. ATWATER.

Please address replies to F. W. Clarke, U. S. Geological Survey, Washington, D. C., U. S. A.

COMMITTEE ON COAL ANALYSIS.

During the past year directions for coal analysis have been formulated for discussion by the committee but, owing to the difficulty which some members of the committee find in securing time for such work, little progress has been made. It is hoped that a more satisfactory report can be made in December.

Respectfully submitted,

W. A. NOYES,  
W. F. HILLEBRAND,  
CHAS. B. DUDLEY.

CHANGES OF ADDRESS.

Burk, W. E., 937 N. 7th St., Terre Haute, Ind.  
Chamberlin, W. E., 22 Van Winkle St., Jersey City, N. J.  
Dabney, Charles W., Univ. of Tenn., Knoxville, Tenn.  
Foster, Wm., Jr., 166 Nassau St., Princeton, N. J.  
Nagelvoort, J. B., 127 Elmwood Ave., Detroit, Mich.  
W. M. Pope, 30 Tiffany Pl., Brooklyn, N. Y.  
White, Alfred H., 413 E. Liberty St., Ann Arbor, Mich.  
Woolworth, J. G., 435 Angell St., Providence, R. I.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

A special meeting of the New York Section was held at the College of the City of New York, on Friday evening, October 1st, to entertain Prof. Henry E. Armstrong, of London. Prof. Armstrong addressed the meeting on methods of teaching chemistry, Messrs. Doremus, Bolton, Loeb, Hale, and Fay taking part in the discussion. A vote of thanks to Prof. Armstrong was moved, seconded, and carried. Dr. H. C. Bolton spoke for thirty minutes on the "Revival of Alchemy." Dr. Doremus invited the members to inspect a large Holtz machine in the college laboratory before leaving the building, after which the meeting adjourned.

MARSTON T. BOGERT, Sec. *pro tem.*

The annual meeting of the New York Section was held in the Chemical Lecture Room of the College of the City of New York, on Friday evening, October 15th, with fifty-two members present,

Dr. Wm. McMurtrie presiding. The minutes of the special meeting of October 1st were read, corrected, and accepted.

The treasurer of the section made his report, after which the election of officers for the ensuing year took place, resulting as follows : Chairman, Dr. Wm. McMurtrie ; Secretary and Treasurer, Durand Woodman ; Executive Committee, A. C. Hale, C. A. Doremus, A. A. Breneman ; Delegates to the Scientific Alliance, Marston T. Bogert, C. F. McKenna.

The death of Dr. M. Alsberg was then formally announced, and an obituary notice by Dr. H. Endemann was read by the secretary.

The following papers were read :

" Some Experiments in Thermo-Electric Pyrometry." By Parker C. McIlhiney.

" Some Records of Recent Progress in Industrial Chemistry." By Dr. Wm. McMurtrie.

A unanimous vote of thanks was passed to the chairman for his efforts in behalf of the section during the year, after which the meeting was adjourned.

DURAND WOODMAN, Secy.

**Issued with December Number, 1897.**

## **Proceedings.**

### **NAMES PROPOSED FOR MEMBERSHIP.**

Fenner, Albert, Jr., 869 Westminster St., Providence, R. I.  
Steel, Frederick Wm., care Fiji Sugar Co. Ltd., Tamuna,  
Narna, Fiji.  
Harper, Dr. Chas. A., 2139 Gilbert Ave., Cincinnati, O.  
Richardson, Clifford, care Barber Asphalt Paving Co., Long  
Island City, N. Y.  
Mitchell, Robert H., 711 Sutter St., San Francisco, Cal.  
Whitaker, De Berniere, Sparrows Point, Md.  
Babcock, Stephen C., Ill. Steel Co., South Works, Chicago.  
Pessolt, H. A., Ill. Steel Co., North Works, Chicago.  
Pendleton, Prof. Hunter, Lexington, Va.  
Simons, Frank D., 1749 Madison St., Washington, D. C.  
Fell, Joseph W., 235 12th St., Washington, D. C.  
Ely, Charles Russell, Gallaudet College, Washington, D. C.  
Thigpen, John Howard, Columbian Univ., Washington, D. C.  
Portner, Edward S., 1104 Vermont Ave., Washington, D. C.  
Spieler, August J., care Emery Candle Co., Ivorydale, O.

### **CHANGES OF ADDRESS.**

Battle, H. B., Winston, N. C.  
Beecher, Jesse B., 1309 Nebraska St., Sioux City, Iowa.  
Benjamin, Dr. Marcus, U. S. Nat. Mus., Washington, D. C.  
de Benneville, Jas. S., 1716 Pine St., Philadelphia, Pa.  
Blasdale, W. C., 2614 Channing Way, Berkeley, Cal.  
Briggs, T. Lynton, care Am. Pegamoid Co., Undercliffe, Ber-  
gen Co., N. J.  
Burk, W. E., 937 N. 7th St., Terre Haute, Ind.  
Cutts, H. E., 242 State St., Portland, Maine.  
Dortch, F. W., 813 Demonbreun St., Nashville, Tenn.  
Edgar, C. G., 565 Woodward Ave., Detroit, Mich.  
Emmens, Dr. S. H., 1 Broadway, N. Y. City.  
Fassett, Chas. M., 114 Mill St., Spokane, Wash.  
Fireman, Dr. Peter, Columbian Univ., Washington, D. C.  
Forbes, Fred. B., 92 Orchard St., W. Somerville, Mass.  
Ford, Allen P., 52 Judd St., Chicago, Ill.  
Fullam, Frank L., Round Mountain, Ala.  
Fuller, Geo. W., 549 Third St., Louisville, Ky.  
Hand, Daniel, 14 Saybrook Place, Newark, N. J.  
Harsh, S. A., Box 804, Helena, Mont.

N. Monroe Hopkins, 2140 Florida Ave., N. W., Washington,  
D. C.  
 Hoskins, William, Room 55, 81 So. Clark St., Chicago, Ill.  
 Jameson, A. H., Cleveland Linseed and Oil Co., So. Chicago,  
Ill.  
 Kendall, E. Dwight, 177a St. James Place, Brooklyn, N. Y.  
 Kiefer, H. E., 438 Cherokee St., So. Bethlehem, Pa.  
 Mackay, P. A., 288 Fifth St., LaSalle, Ill.  
 Marlatt, Miss Abby L., Man. Tr. High School, Providence,  
R. I.  
 Michaelis, Gustavus, 541 Western Ave., Albany, N. Y.  
 Parmelee, C. W., cor. Green and West Sts., Brooklyn, N. Y.  
 Pease, F. N., Box 210, Altoona, Pa.  
 Redding, Allen C., Baker City, Oregon.  
 Rosengarten, Geo. D., 1700 Fitzwater St., Philadelphia, Pa.  
 Schiller, Louis J., care Arbuckle Bros., Foot of Pearl St.,  
Brooklyn, N. Y.  
 Shaw, W. T., Gilt Edge, Mont.  
 Smalley, F. N., Westboro, Mass.  
 Stiles, Wm. M., 351 First St., Brooklyn, N. Y.  
 Stone, Geo. C., The N. J. Zinc Co., Newark, N. J.  
 Thatcher, R. W., 735 No. 13th St., Lincoln, Nebr.  
 Walker, Henry V., 21 Cliff St., N. Y. City.  
 Yates, J. A., Ottawa Univ., Ottawa, Kans.

## ADDRESS WANTED.

Sims, Clough, formerly of 20 Morris Hall, Ithaca, N. Y.

## NEW YORK SECTION.

The November meeting of the New York Section was held November 5th at the College of the City of New York, Dr. Wm. McMurtrie in the chair.

The minutes of the previous meeting were read, corrected, and accepted.

Formal announcement was made of the death of Prof. Charles E. Colby, of Columbia University, and of a necrological notice to be read by Prof. M. T. Bogert at the December meeting.

The following papers were read: "Corrected Assays," by E. H. Miller; "The Chemistry of Formaldehyde in Disinfection with Exhibits," by E. J. Lederle, read by Mr. J. A. Deghuée in the author's absence.

In the discussion which followed, methods of determining the

strength of formaldehyde solutions were described and their deficiencies pointed out. Mr. J. C. Boot preferred the potassium hydroxide method owing to the sharper end-reaction, and described the procedure as follows:

"In a glass-stoppered flask fifty cc. normal potassium hydroxide are heated with five cc. formaldehyde solution for two hours at 85° C. The excess of potassium hydroxide is titrated with normal hydrochloric acid using phenolphthalein as indicator.

"Two molecules of formaldehyde and one molecule potassium hydroxide, giving one molecule potassium formate and one molecule methyl alcohol:  $2\text{CH}_2\text{O} + \text{KOH} = \text{HCOOK} + \text{CH}_3\text{OH}$ . The method is accurate and the titration very sharp."

Mr. H. H. Fries considered the two hours' heating a source of loss and error, in which Mr. Sohon concurred, and both preferred the ammonia method.

The effect of formaldehyde on glue, gelatin, and albuminoids was discussed, the weight of opinion being that gelatin is rendered permanently insoluble, although the experience of some was not entirely in accord with this view, probably on account of imperfect drying of the samples operated on.

The chair announced, for the next meeting, a paper on the "Chemistry of Substances Used in Perfumery," and expressed the hope that it would arouse as interesting and active a discussion as had followed Dr. Lederle's paper.

The meeting then adjourned.

DURAND WOODMAN, *Secretary.*

#### CINCINNATI SECTION.

The October meeting of the Cincinnati Section took place October 15th in the Chemical Lecture Room of Hanna Hall, University Buildings, Dr. Alfred Springer in the chair.

Mr. L. O. LaBach was elected a member of the section.

Dr. Chas. A. Harper gave an interesting talk on his visit to the city of Canton, China.

Miss Hannah L. Wessling demonstrated the production of hydrobromic and hydriodic acids as a lecture experiment according to the methods proposed by Kastle and Bullock, which are based upon the action of bromine upon naphthalene, and of iodine upon colophony respectively.

Prof. Norton and Dr. Springer then gave an account of the papers read at the meeting of the British Association for the Advancement of Science at Toronto, and of the more general features of the meeting.

On motion the meeting adjourned.

The November meeting of the Cincinnati Section was held on Tuesday, Nov. 16, in the Lloyd Library, 22 members being present, Dr. Alfred Springer in the chair.

Mr. F. J. Barringer and Dr. R. M. McKenzie were elected members of the section.

Prof. James Lewis Howe contributed a paper entitled "Some New Ruthenocyanides and the Double Ferrocyanides of Barium and Potassium."

A query was read by the secretary, contributed to the question-box by Mr. J. Henry Schroeder, as follows: "What objections, supported by analytical data, may be cited, why the assay of alkaloidal drugs in general should not be conducted by a uniform process, by the use of Prolli's fluid, or a modification thereof?" The question, in view of its scope, was left open for some future response. In a brief discussion, the evanescence of some alkaloids was touched upon, especially of cocaine in prolonged contact with ammonia water in aqueous solution.

Dr. S. P. Kramer then read an interesting paper "On the Fat-forming Function of the Blood," an experimental investigation which the author intends to continue.

Finally the proposed new constitution was made the subject of discussion. The section abstained from adopting a resolution with regard to the proposed constitution.

On motion the meeting adjourned.

S. WALDBOTT, *Secretary.*

#### NEBRASKA SECTION.

The meeting was called to order at 8.25 P.M., October 29, President Nicholson in the chair.

The president made a statement of the aims and objects of the section and of eligibility for membership for the benefit of those in the audience who might be interested enough to care to join.

The minutes of the previous meeting were read and approved.

Dr. Senter gave a brief historical account, interspersed with numerous personal recollections of the life, work, and death of Victor Meyer. Dr. White read a short obituary notice of Professor Fresenius.

Miss Bouton read a paper upon the action of chlorine and of bromine upon ethylbenzol. This paper will shortly appear in the journal of the society.

JOHN WHITE, *Secretary.*

